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## User Data Package UDP-2001-ENV

### USER DATA PACKAGE AND OPERATION TEST REPORT FOR THE IMPLEMENTATION OF THE SODIUM SULFIDE/ FERROUS SULFATE PROCESS AT NAVY IWTPS

by

Edward R. Durlak


February 1997

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13. ABSTRACT (Maximum 200 words)  The ferrous sulfate/sodium sulfide (FS/SS) process is a treatment technology for the reduction of hexavalent chromium and precipitation of heavy metals in industrial wastewater treatment plants (IWTPs). When the ferrous ion, as ferrous sulfate, is mixed with sulfide, the hexavalent chromium is rapidly reduced to its trivalent state at a neutral pH and then precipitated. FS/SS technology can be used to replace the current hydroxide treatment chemistry. This report presents the results and lessons learned from full-scale implementation of FS/SS. The FS/SS treatment process reduced the volume of sludge generated by 20 to 30 percent, reduced the amount of treatment chemicals, and resulted in over \$35,000 annual savings. Furthermore, metal sulfides tend to be two to three orders of magnitude less soluble than their corresponding metal hydroxides. This gives cleaner effluent, which helps the facility meet environmental requirements. Further benefits include the removal from the shop area of the high pressure sulfur dioxide cylinder (used in the hydroxide process), a faster and more reliable chrome reduction method, neutral pH operation that extends tank and equipment life, and less acid and caustic chemicals stored on the shop floor. As Navy activities do more with less, the FS/SS process can help meet increasingly stringent standards.				
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IMPLEMENTATION  
OF THE SODIUM SULFIDE/FERROUS SULFATE  
PROCESS AT NAVY IWTPs

Demonstration accomplished under:  
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## EXECUTIVE SUMMARY

Navy Industrial Wastewater Treatment Plants (IWTPs) receive wastewater from paint stripping, parts cleaning and electroplating operations. These wastewaters typically contain high concentrations of heavy metals, such as, trivalent ( $\text{Cr}^{+3}$ ) and hexavalent ( $\text{Cr}^{+6}$ ) chromium, cadmium, copper, lead, nickel, silver and zinc as well as complexing agents, surfactants, oils and greases. The influent wastewater to the IWTP must be treated to precipitate out the metals to meet existing EPA discharge limits.

Several processes exist that can precipitate the heavy metals out of the wastewater. However,  $\text{Cr}^{+6}$  must first be reduced to  $\text{Cr}^{+3}$  before precipitation can occur. The most common method uses sulfuric acid to reduce all the wastewater to a pH of between 2 and 3, sulfur dioxide or sodium sulfite/bisulfite to reduce the chromium, and caustic or lime to raise the pH of the wastewater above 9 to effectively precipitate all the metals as hydroxides. This User Data Package (UDP) includes planning, design, installation, and operation and maintenance requirements for using an alternate method, the Sodium Sulfide/Ferrous Sulfate (SS/FS) method. The SS/FS process precipitates all the metals as sulfides (except that chrome precipitates as a hydroxide) at a neutral or slightly alkaline pH between 7 and 8. The SS/FS process uses less costly chemicals and produces less hazardous sludge to offer cost savings over other commonly used processes.

The IWTP at the Naval Undersea Warfare Center (NUWC) at Keyport, WA, was selected for a full scale demonstration of the SS/FS process. The IWTP had been using the sulfuric acid/sulfur dioxide/caustic process for treating their industrial wastewaters. Jar tests conducted at the IWTP indicated that the SS/FS process could remove all of the heavy metals to well below the plant discharge requirements and cost savings were estimated at 38%. Based on the jar tests and prior pilot plant tests conducted at NAS Pensacola, feeds of chemicals were optimized and the design modifications were implemented at NUWC Keyport. The IWTP was started up using the SS/FS process in September 1995.



Several start up and operational problems necessitated temporarily reverting to the old caustic process for about a month while the problems were resolved. One of these problems involved the storage tank mixer operation that caused the iron to be oxidized from ferrous to ferric and sulfide to sulfate so that true SS/FS operation was circumvented. Other problems involved interference of phosphates/detergents in the wastewater, optimum polymer selection for excellent clarification and several routine maintenance problems.

All the initial start up and operational problems have been resolved and the SS/FS process has been in operation at NUWC Keyport for nine months. During this period, the SS/FS process treated NUWC wastewater with hexavalent chromium as high as 310 mg/L while easily meeting current and proposed EPA discharge limits. For the entire nine months of operation, a cost comparison of the SS/FS process with the Sulfuric Acid/Sulfur Dioxide/Caustic process indicated a 59% reduction in the cost of chemicals and a 31% reduction in sludge disposal costs. On an annual basis, total cost savings amounted to \$31,950 or 34% over the old treatment process. At high concentrations of  $\text{Cr}^{+6}$  (up to 100 mg/L), the sludge generation and disposal costs savings were reduced to 17%.

The SS/FS process offered several additional advantages to NUWC Keyport over the conventional process they had used and these are:

- A significant advantage of the SS/FS process is that all metals, except chromium, are precipitated out as sulfides which are orders of magnitude less soluble in water than metal hydroxides precipitated in the conventional process. Hence, the SS/FS process can easily meet current EPA NPDES discharge limits and the more severe limits that may be proposed in the future.
- Hexavalent chrome reduction does not become limited at low concentrations of 0.1 mg/L or less as it does with conventional processes.

- Since the reduction of  $\text{Cr}^{+6}$  is instantaneous with the SS/FS process compared with a retention time of 45 minutes minimum with the conventional process, a multiplicity of large retention tanks are not required and a considerable savings of space and cost of structures can result.
- The reduction in processing time will enable the Keyport IWTP operators to treat and clarify batch sizes of 39,000 gallons of wastewater in one shift per day.
- Because the SS/FS process reduces chrome at near neutral pH (the optimum was 7.6) as compared with 2 to 3 with the conventional process, less acid and caustic had to be purchased and stored on site.
- Operation at neutral pH instead of at acidic conditions also reduce tank corrosion and increase tank life.
- The SS/FS process operation at the NUWC Keyport IWTP was able to reduce all  $\text{Cr}^{+6}$  that could slip through with the cyanide plant effluent, unlike the conventional process operation, thus avoiding potential violations of the discharge limits. The reason for this is that the conventional process does not treat the wastewater for  $\text{Cr}^{+6}$  reduction if no  $\text{Cr}^{+6}$  is shown to be present. The SS/FS process always treats for  $\text{Cr}^{+6}$ , even if none is shown to be present.
- Implementation of the SS/FS process at NUWC Keyport allowed the disposal of two large  $\text{SO}_2$  tanks, thus eliminating a safety hazard at the IWTP.
- Microfiltration instead of clarification can easily be incorporated with the SS/FS process, thus eliminating use of expensive polymers and minimizing the IWTP size.

The IWTP personnel at NUWC Keyport have been pleased with the operation of the SS/FS process and intend to continue to use it in the future. It is recommended that the SS/FS process be implemented at other Navy IWTPs so that even more stringent discharge limits can be met and similar or larger cost saving can be achieved.

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## 1.0 INTRODUCTION

### 1.1 OBJECTIVE

The Sodium Sulfide/Ferrous Sulfate (SS/FS) process is a process for the reduction of hexavalent chromium ( $\text{Cr}^{+6}$ ) to trivalent chromium ( $\text{Cr}^{+3}$ ) and precipitation of heavy metals such as cadmium, chromium, copper, lead, nickel, and zinc from industrial wastewater generated in degreasing, paint stripping, and electroplating metal processing operations. The process results in a reduction in the quantity of sludge generated and can be used to remove heavy metals from Navy IWTP wastewater in a more efficient, less costly manner than existing methods.

The SS/FS process was initially evaluated for application to industrial wastewater treatment at the Public Work Center, Pensacola, FL (Reference 1 and 2). The process, however, was not implemented at Pensacola since the Pensacola IWTP would no longer be receiving heavy metal bearing industrial wastewater. The objectives of the program are to:

- Determine the applicability of the SS/FS metal precipitation process to treatment of the heavy metal bearing industrial wastewater at the Naval Undersea Warfare Center (NUWC), Keyport, WA, and other Navy bases.
- Determine the chemical feed and operational requirements for implementation of the process.
- Perform the plant upgrades required to evaluate the process in place of the currently used Sulfuric Acid/Sulfur Dioxide/Caustic (sodium hydroxide - NaOH) treatment process.
- Start-up and demonstrate the process at the NUWC Industrial Wastewater Treatment Plant (IWTP).
- Determine the amount of sludge reduction and cleanliness of the effluent in meeting discharge requirements using the new process.

The SS/FS process can easily and economically be implemented into existing wastewater treatment plants. The modifications required for the NUWC IWTP would generally be the same as required for other existing facilities (see Section 4.0 and 8.2). NFESC can provide technical support to help evaluate potential implementations.

## **1.2 BACKGROUND**

In the metal finishing industry, the surface of the metal may require preparation prior to applying a finish to the surface. Preparation techniques range from acid washes to complex, multi-stage chemical cleaning processes. Processes for preparing metal for electroplating could involve acid pickling for scale removal and several stages of alkaline cleaning. Following each process, the parts are rinsed. Most carbon steels and stainless steels are pickled using sulfuric, hydrochloric or hydrofluoric acids. Most alkaline cleaning solutions contain alkali hydroxides and carbonates, organic/inorganic additives and surfactants. Alkaline cleaning is often assisted by ultrasonics or by electric potential.

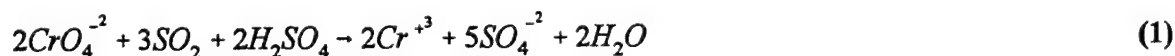
Anodizing is an electrolytic process that converts the metal surface to an insoluble oxide coating. Anodized coatings provide corrosion protection, a base for other coating processes and special electrical and mechanical properties. Aluminum is the most common anodized material and this process may include chromic acid, sulfuric acid and boric acid anodizing. Following anodizing, the parts are rinsed and sealed using chromic acid, nickel acetate, nickel-cobalt acetate and hot water.

The electroplating process includes degreasing, alkaline cleaning, electrocleaning, anodizing, and electrochemical deposition of the protective metal. The process metals and chemical solutions are then carried into the wastewaters which must be treated in the wastewater treatment plants (Reference 3). Other wastewaters are produced from cleaning processes. The wastewaters contain heavy metals, including hexavalent chromium, cadmium, chromium, copper,

lead, nickel, and zinc, as well as, complexing and chelating agents, surfactants or soaps, and oils, and greases. The wastewaters must be treated to remove the contaminants prior to discharge.

In 1980, metal-bearing sludges generated at all industrial wastewater treatment facilities were classified as hazardous in accordance with regulations issued by the Environmental Protection Agency (EPA). These sludges require special handling and disposal in hazardous waste landfills (Reference 3). Such disposal is costly. Reduction of water flow rate and pollutant loading will decrease the use of treatment chemicals and choice of treatment chemicals will determine the quantity of solid waste requiring disposal (Reference 4). Process changes are being implemented to minimize such wastewater contaminants as cyanides (Reference 5). The common treatment for metal finishing wastewater consists of oil and grease separation, followed by destruction of cyanides, neutralization, separation of the metal hydroxides, and finally, sludge disposal (Reference 6).

Hexavalent chromium cannot be precipitated without prior reduction to trivalent chromium. Reduction with sulfur dioxide is the method used most commonly on a large scale (Reference 7). The reduction reaction using sulfur dioxide is:



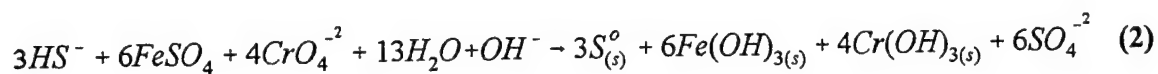
Other methods of acidic reduction include the use of sodium sulfite, sodium bisulfite, and ferrous compounds. Hexavalent chromium reduction with sulfur dioxide (or similar reducing compounds) theoretically requires a 3:2 ratio as shown in Equation 1 above. A 1:2 ratio, however, is applicable for sulfide-hexavalent chromium reduction. The quantity of sludge produced by the different reducing agents can vary dramatically.

Sulfur compounds ( $S^{+4}$ ) can reduce hexavalent chromium at pH less than 3. The rate slows logarithmically with increased pH. Sulfides ( $S^{-2}$ ) also reduce hexavalent chromium at acidic

pH. Sulfides convert to hydrogen sulfide gas at acidic conditions and the latter is released as a toxic gas if not confined to the aqueous medium. Under closed conditions, and with the use of peroxide for oxidation of the residual sulfide before discharge, an acidic sulfide process is effective for reduction of hexavalent chromium (Reference 3). In the neutral or alkaline pH range, the reaction rate, however, is unacceptably slow.

Ferrous ion is not efficient, by itself, in reducing hexavalent chromium since only one electron is available per iron atom and a large quantity of iron hydroxide sludge is produced. However, the ferrous ion can reduce hexavalent chromium at alkaline pH by itself, is an effective coagulant, and is required as a catalyst if sulfide is used as a reducing agent at neutral pH.

When the ferrous ion, as ferrous sulfate, is present together with sulfide, the hexavalent chromium is rapidly reduced at neutral and alkaline pH. The theoretical basis for ferrous and sulfide reduction of hexavalent chromium is based on the 1983 report by Higgins and Sater (Reference 8). The ferrous ion appears to catalyze the sulfide reaction. Near a pH of 8.5 to 10, the effectiveness of the sulfide ion is reduced. At this pH, the ferrous ion ( $Fe^{+2}$ ) is converted to the ferric ion ( $Fe^{+3}$ ). At neutral pH, the proposed reaction for equivalent doses of ferrous ion and sulfide is (Reference 8):



This reaction would be favored slightly by an increase in pH. Increasing the ratio of the sulfide to ferrous ion reduces the effect of increased pH. Ferrous ion and sulfide appears to be the best combination for reducing and removing hexavalent chromium at neutral or near neutral conditions.

According to the literature, the ferrous iron serves as a catalyst in the reaction of the sulfide with hexavalent chromium to produce the trivalent chromium. By definition of a catalyst, this is not true as the ferrous iron does participate and is changed in the reaction, becoming ferric

iron. As a true catalyst, the ferrous iron would be available for reuse. This is not true for the SS/FS process, since it is not available for reuse. Ferrous iron will reduce the hexavalent chromium at neutral pH. The reaction, however, is slow and theoretically the reaction requires six ferrous ions to occur. In actual practice, however, approximately 12 ferrous ions are required to reduce each hexavalent chromium ion. This generates a significant amount of sludge.

Sulfide, alone, will not reduce the hexavalent chromium at neutral or basic pH. It is reported that the presence of the other heavy metals will help catalyze the reaction. During Phase I testing at of the SS/FS process, a number of different tests were run with the other heavy metals present and without iron to determine if chromium reduction does occur. There was no change in the concentrations of the hexavalent chromium with sulfide and the other heavy metals present, even when allowed to react 24 hours.

Chromium reduction with sulfide will occur if the iron is present as the ferric ion. However, the clarification and settling is not as good as when the ferrous iron is used. The optimum sulfide and ferrous concentrations are near the theoretical concentrations, as shown in equation 2. These are the values where chromium is reduced and good settling and clarification does occur. Chromium reduction will occur at lower iron concentrations with higher sulfide concentrations. The precipitate formation and clarification is not as efficient at these higher sulfide concentrations. At high ratios of sulfide to ferrous and hexavalent chromium, although chromium reduction does occur, the precipitate is extremely fine ( $<0.45 \mu\text{m}$ ) and settling does not occur. In this respect, the ferrous iron (ferric iron) is also acting as a coagulant. However, as a coagulant, iron or alum are normally added at concentrations of 50 to 200 mg/L. At low influent hexavalent chromium concentrations (1 to 20 mg/L), the ferrous ion is only added at 1.5 to 30 mg/L, which is much less than a normal coagulant.

The standard applied treatment technology for removal of heavy metals is chemical precipitation, generally as the hydroxide. Precipitation is essentially complete for copper, zinc, iron, manganese, nickel, and cobalt. Cadmium, mercury, and lead may require soda ash or sodium

sulfide for precipitation (Reference 9). Chlorination may be needed to destroy complex organic metallic compounds (such as cyanide) prior to precipitation. Other methods of removal include electrodeposition, reverse osmosis, solvent extraction, ultrafiltration, ion exchange, and activated carbon adsorption. In hydroxide precipitation, sludge from the clarifier will contain up to 3 percent solids, depending on the settling time. Further dewatering will produce a sludge containing 12 - 18 percent solids (Reference 10).

Most metal hydroxides have a relatively high solubility, with increased solubility of the metal hydroxide complex at high pH. Many of the metal hydroxide precipitates are amphoteric in nature and dissolve at high pH values due to reaction (4) where M is the metal ion (Reference 11)



Hydroxide precipitation of all heavy metals present cannot be relied on because the minimum solubilities of the various metals do not occur at the same pH. In addition, the presence of complexing agents or soaps hinders effective precipitation (Reference 12 and 13).

The hydroxide process generally removes metals down to 1 or 2 mg/L (Reference 10). The metal sulfides tend to be at least 4 or 5 orders of magnitude less soluble than their corresponding metal hydroxides (Table 1, Reference 12). As the discharge requirements for industrial and metal finishing wastewaters are decreased, the hydroxide process will no longer be able to meet the limits, whereas, sulfide precipitation will meet these lower discharge requirements.

Metal precipitation by soluble sulfides require a sulfide source more soluble than the metal to be precipitated such as sodium sulfide (Reference 13). Sodium sulfide disassociates readily into sodium and sulfide ions as follows:



Table 1.		
Solubilities of Metal Hydroxides and Sulfides (Reference 12).		
Metal	$k_{sp}$ Hydroxide	$k_{sp}$ Sulfide
Manganese	1.2	$2.1 \times 10^{-3}$
Iron (II)	$8.9 \times 10^{-8}$	$3.4 \times 10^{-5}$
Zinc	1.1	$2.3 \times 10^{-7}$
Nickel	$6.9 \times 10^{-3}$	$6.9 \times 10^{-8}$
Tin (II)	$1.1 \times 10^{-4}$	$3.8 \times 10^{-8}$
Cobalt	$2.2 \times 10^{-1}$	$1.0 \times 10^{-8}$
Lead	2.1	$3.8 \times 10^{-9}$
Cadmium	$2.3 \times 10^{-5}$	$6.7 \times 10^{-10}$
Silver	13.3	$7.4 \times 10^{-12}$
Copper	$2.2 \times 10^{-2}$	$5.8 \times 10^{-18}$
Mercury	$3.9 \times 10^{-4}$	$9.0 \times 10^{-20}$
Chromium does not precipitate as a sulfide		

Under acidic conditions, the free sulfide can react with the water to form free hydrogen sulfide gas or can react to precipitate a heavy metal. At neutral pH or alkaline conditions, the formation of hydrogen sulfide is avoided and metal sulfide precipitation occurs as follows:



Advantages of the sulfide process are the very low solubilities of most metal sulfides, the sulfide ability to reduce hexavalent chromium at neutral or basic pH in the presence of the ferrous ion, and its increased ability to precipitate metals that are complexed with at least some of the weaker complexing agents. The problem of odor and toxicity of hydrogen sulfide does not exist

under normal alkaline operating conditions (Reference 10). Personnel and operation precautions should always be practiced with the use of sulfide chromium reduction or with sulfur dioxide chromium reduction. The high reactivity of sulfides ( $\text{HS}^-$ ,  $\text{S}^{2-}$ ) with heavy metal ions and the low solubility of heavy metal sulfides over a broad pH range are attractive features when compared to the corresponding hydroxide precipitation processes (Reference 12) where each metal hydroxide's minimum solubility occurs at a different pH (Figure 1).

The Air Force Engineering & Services Center Report, ESL-TR-87-39, contains an extensive literature review describing the kinetics and chemistry of the reduction process of hexavalent chromium species and the metal precipitation processes (Reference 14). Under funding from the Air Force Engineering & Services Center, Tyndall AFB, the SS/FS method of reducing hexavalent chromium and removal of the heavy metals from electroplating and industrial wastewater was technically verified by laboratory tests, pilot field tests, and full-scale implementation of the process in the existing Industrial Wastewater Treatment Plant (IWTP) at Tinker AFB, OK (References 15, 16, and 17). The SS/FS process was patented by the United States Air Force (Reference 18). The Air Force granted Environmental Research and Development, Inc. (ERAD) an exclusive license to the process for commercial application. There are no restrictions on the government use of the process.

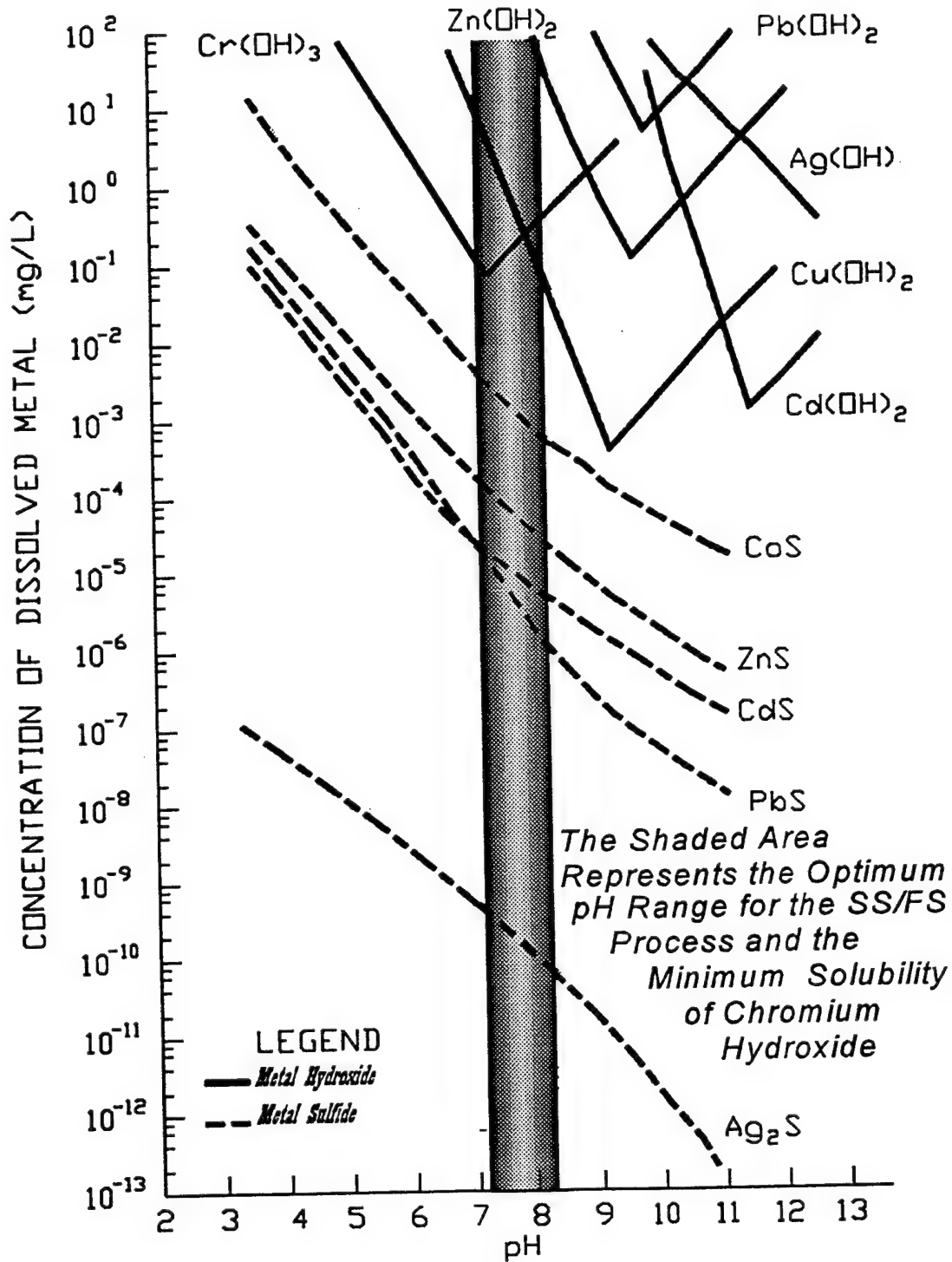
The SS/FS process was evaluated for application to industrial wastewater treatment at the Public Work Center, Pensacola, FL (Reference 1 and 2). Phase I included evaluation of the wastewater chemistry through wastewater analysis, jar testing and review of the available analytical and process data and design of a pilot test facility (Reference 1). Phase II was pilot scale testing to optimize the chemical parameters for the SS/FS process. The pilot scale testing included optimizing the sodium sulfide, ferrous sulfate, and polymers required for heavy metal removal from the influent industrial wastewater at the facility (Reference 2).

The SS/FS process was compared to the Sulfuric Acid/Sulfur Dioxide/Lime process at influent hexavalent chromium concentrations of 1 to 100 mg/L  $\text{Cr}^{+6}$ . With the Sulfuric Acid/



FIGURE 1

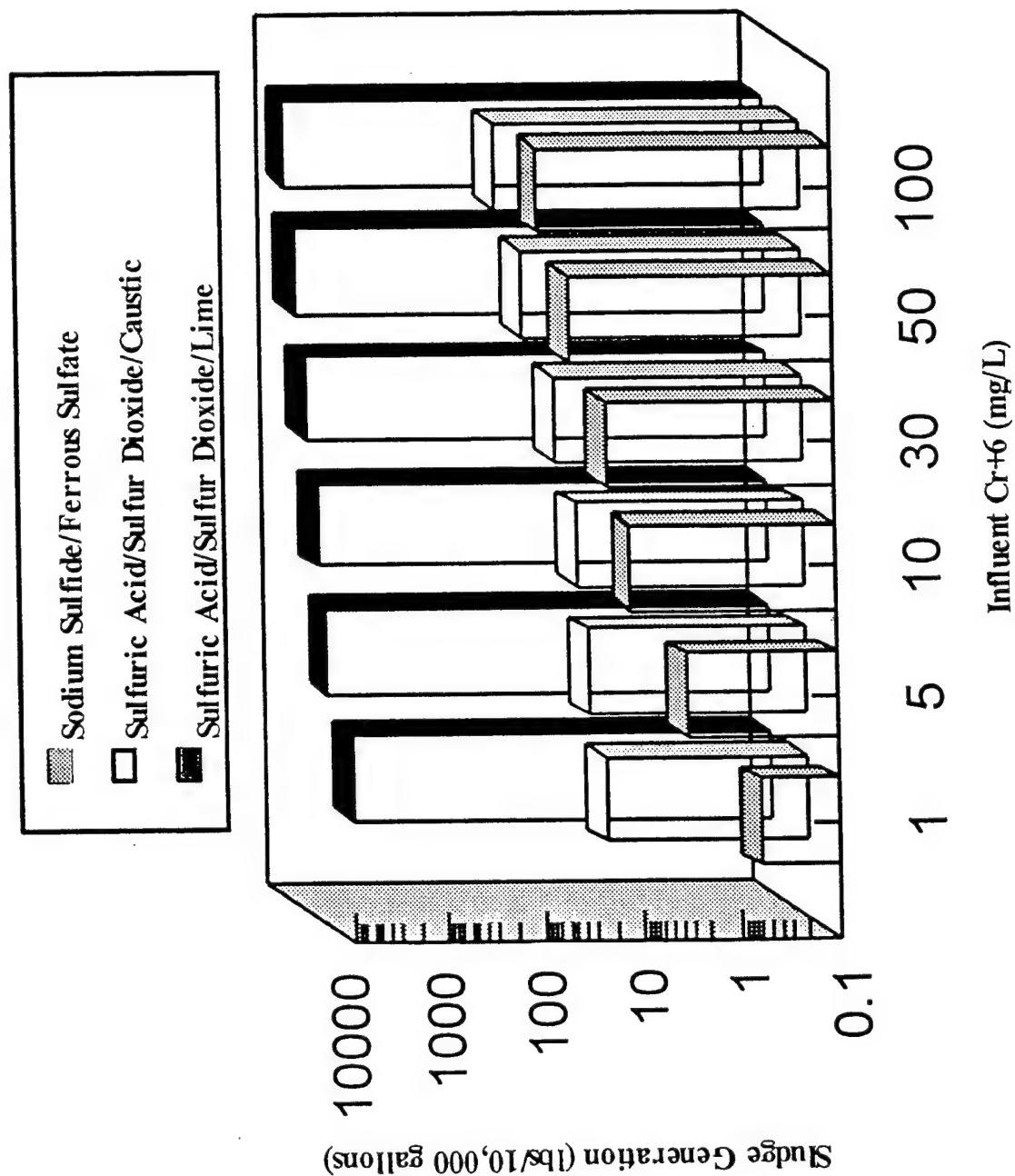
METAL SULFIDE SOLUBILITY



Sulfur Dioxide/Lime process, the lead and copper concentrations in the treated effluent were greater than discharged requirements (Reference 2). The total treatment and sludge disposal cost for the SS/FS process increased from approximately \$10/10,000 gallons of wastewater at 10mg/L Cr<sup>+6</sup> to \$60/10,000 gallons of wastewater at 100 mg/L Cr<sup>+6</sup> as shown in Table 2. The total treatment and sludge disposal cost for the sulfuric acid/sulfur dioxide/lime process increased from approximately \$130/10,000 gallons of wastewater to \$350/10,000 gallons of wastewater at the same Cr<sup>+6</sup> levels. The SS/FS process met all metal discharge requirements. Figure 2 shows the sludge generation for the H<sub>2</sub>SO<sub>4</sub>/SO<sub>2</sub>/Lime, H<sub>2</sub>SO<sub>4</sub>/SO<sub>2</sub>/Caustic and the SS/FS metal precipitation processes.

<b>Table 2.</b> <b>Treatment and Sludge Disposal Cost Comparison of the Sodium Sulfide/Ferrous Sulfate Process Versus the Sulfuric Acid/Sulfur Dioxide/Caustic Process.</b>	
Influent Cr+6 (mg/L)	Treatment Cost (\$/10,000 gallon)
<b>Sodium Sulfide/Ferrous Sulfate Process</b>	
10	\$ 10
100	\$ 60
<b>Sulfuric Acid/Sulfur Dioxide/Lime Process</b>	
10	\$130
100	\$350

The SS/FS process was evaluated for application to the Albany, GA Marine Corps Logistic Base Industrial Wastewater Treatment Facility (Reference 19). Jar test evaluation of the process in comparison to the existing Sulfuric Acid/Sulfur Dioxide/Caustic precipitation process (chromium reduction/metal precipitation process similar to the process at the NUWC) showed a cost savings of approximately 90 percent in chemical usage and 15 percent in sludge reduction could be realized with the implementation of the process. In addition, the current caustic precipitation process does not always result in lead removal to discharge requirements. The SS/FS process readily removed the lead to discharge requirements. Currently, the process is being implemented at the Albany, GA Marine Corps Logistic Base.



**Figure 2.** The Sludge Generation as a Function of the Influent Hexavalent Chromium Concentration.

### 1.3. SCOPE

The purpose of this project was to evaluate the environmental and economic impact of the demonstration/implementation of the SS/FS process at the NUWC, Keyport, WA and if economic, implement the process at the facility. The program included evaluation of the wastewater chemistry through wastewater analysis, jar testing and review of the available analytical and process data, and evaluation of the unit processes of the waste treatment facility to determine the applicability of the SS/FS metal treatment process for heavy metals removal at the facility. Preliminary process economics were determined with the jar testing. The project included the completion of the plant modifications required for process demonstration, preparation of a process Operation and Maintenance Manual, process training and full-scale implementation and startup of the process at the NUWC. Economics of the process were determined during process operation. The economics were based on the chemical requirements, the processing time, efficiency, effectiveness, and the sludge generation during plant operation.

This User Data Package describes the results of the jar testing, full scale operation, and requirements for process implementation.

## 2.0 WASTEWATER TREATMENT PLANT PROCESS DESCRIPTION

The industrial wastewater treatment plant for the NUWC is designed as a batch treatment plant (Figure 3). Currently, 36,000 to 38,000 gallons of wastewater is treated per batch. The wastewater is received in two 40,000 gallon holding tanks. When wastewater is not being treated, the wastewater is received separately in the two holding tanks from two separate processing units and the volume of water received from the separate units are recorded. When sufficient volume has been received that treatment is required, the wastewater from Tank 1 is combined into the second tank (the Chrome Waste Reactor Tank) and mixed with recirculation. A third waste stream (the cyanide containing waste) is also received at the plant. This waste is treated for cyanide removal and then fed into the wastestream for heavy metal removal. The volume of each batch of cyanide waste is approximately 7,000 gallons. Table 3 lists some of the data available on the influent wastewater during jar testing. In addition, the wastewater samples collected for jar testing was analyzed for the heavy metals. The results of these analysis are shown in Table 4.

**Table 3.**  
**Keyport NUWC Industrial Wastewater Influent Metal Concentrations.**

Date	Cd (mg/L)	Cr (mg/L)	Cu (mg/L)	Pb (mg/L)	Ni (mg/L)	Ag (mg/L)	Zn (mg/L)	Al (mg/L)	Fe (mg/L)
1/15/91	<1	19	<1	<1	<1	<1	<1	<1	9
7/12/91	3.1	70.7	0.7	0.5	20.7	<1	<1	9.7	24
7/15/91	0.7	49.1	0.6	0.5	3.1	0.1	0.6	11	31.7
7/25/91	0.2	45.6	0.7	0.5	17.3	0.1	0.9	18.1	14
1/14/92	4	18	1	<1	<1	<1	4	7	<1
1/31/92	<1	14	3	<1	<1	<1	1	28	45
5/05/92	<1	38	<1	2	17	<1	<1	15	36
5/06/93	1	1	<1	<1	<	<1	<1	19	13



FIGURE 3 NUWC IWTP PROCESS FLOW DIAGRAM

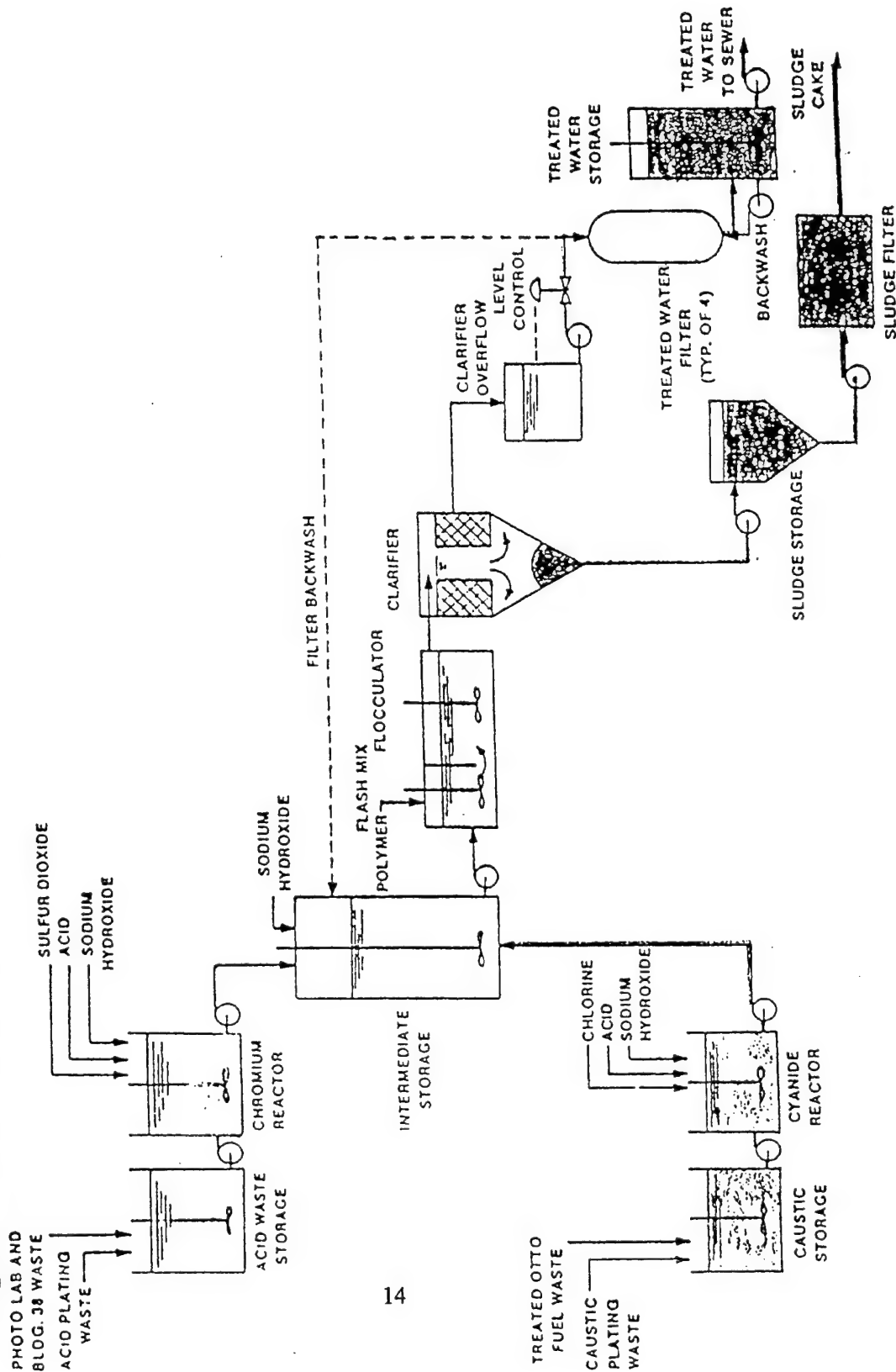


Table 4. Analysis of the Wastewater Samples Used During Jar Testing.		
Constituent	Initial Sample 6/15/94	Initial Sample 6/17/94
Cr <sup>+6</sup> (mg/L)	18	16.75
Total Cr (mg/L)	28	27.5
Copper (mg/L)	0.80	0.10
Iron (mg/L)	2.9	0.50
Nickel (mg/L)	0.005	0.11
Zinc (mg/L)	3.55	0.35
pH (unit)	5.42	5.55

Table 5 lists the monthly flow for June 1993 through May 1994. The influent wastewater is not currently being analyzed for heavy metals. However, in the past, some analysis of the wastewater has been conducted. The two samples collected for jar testing showed an influent hexavalent chromium concentration of 16.75 and 18 mg/L Cr<sup>+6</sup> and a total chromium concentration of 28 and 27.5 mg/L. Plant operations personnel felt this wastewater was fairly representative of what they normally process during treatment. The plant, however, does see variations in the chromium concentration, with considerable increase in the influent hexavalent chromium concentration when anodize strip solutions are processed through the plant. During the plant review meeting, concentrations as high as 500 to 1000 mg/L Cr<sup>+6</sup> were reported. Plant personnel, however, felt these were not normal conditions, and that the normal high concentrations would be 50 to 100 mg/L Cr<sup>+6</sup>. Copper and aluminum is received in the cyanide stream. Iron as ferrous sulfate is added to this stream as a catalyst during cyanide treatment. The variations in the metals concentrations were similar to that for the chromium stream. Duraclean, an aqueous cleaner, is used in the process area and is received in the wastewater. The operators noted that when the Duraclean was present in the wastewater more difficulty in settling the precipitate was observed.

<p align="center"><b>Table 5.</b> <b>Monthly Flow for the Keyport NUWC IWTP</b></p>			
Year	Month	Acid Chrome Line (gallons)	Cyanide Treatment Line (gallons)
1993	June	371,940	21900
1993	July	222,690	21240
1993	August	320,170	20160
1993	September	694,830	27600
1993	October	287,660	22560
1993	November	223,230	9960
1993	December	233,080	16880
1994	January	198,870	27480
1994	February	166,220	11041
1994	March	264,630	0
1994	April	331,530	16080
1994	May	389,220	9840
<b>TOTAL</b>		<b>3,704,070</b>	<b>204,741</b>

To treat the wastewater, the pH of the mixed wastewater is adjusted to 2 to 3 with 12 to 13 percent sulfuric acid in the Chrome Waste Reactor Tank. (The dilute sulfuric acid is made up from 75 percent sulfuric acid.) Sulfuric acid feed is controlled with a pH meter/controller. The operators, however, also control the feed manually and determine the pH of the samples with a laboratory pH meter. Sulfur dioxide gas is fed into the wastewater until chromium reduction has been achieved. The sulfur dioxide feed is controlled via a special injector located in the hazardous gas storage/injector room. Final chromium reduction is confirmed in the laboratory with the colorimetric method for hexavalent chromium. After chromium reduction, the pH is adjusted to pH 8 to 9, typically 8.5 to 9.0, with a 12 to 13 percent caustic solution. (The caustic feed



solution is made up from a 50 percent caustic solution.) The reacted solution is allowed to mix in the Chrome Reactor Tank overnight. The following morning, Betz®1160X cationic polymer is fed into the stream, and the solution is fed through the clarifier. The treated cyanide wastes is combined with the flow prior to clarification. An advantage of the SS/FS process at Keyport is that it also treats the cyanide waste by taking out any metals present. The treated clarifier effluent is filtered with a sand anthracite filter and the pH is adjusted prior to discharge to a Publicly Owned Treatment Works (POTW). The heavy metal discharge requirements for the wastewater are listed in Table 6.

<b>Table 6.</b> <b>Heavy Metal Discharge Requirements for the NUWC IWTP</b>		
	Daily Maximum	Monthly Average
Cadmium (mg/L)	1.0	0.5
Chromium (mg/L)	5.0	2.5
Copper (mg/L)	4.5	1.8
Lead (mg/L)	0.6	0.3
Mercury (mg/L)	0.005	N/A
Nickel (mg/L)	4.1	1.8
Silver (mg/L)	2.0	N/A
Zinc (mg/L)	4.2	1.8

### 3.0 JAR TESTING

#### 3.1 PROCEDURES

Jar tests were conducted using the Phipps & Bird six paddle jar test apparatus. One liter beakers were used. Each beaker was filled with 500 mL of the wastewater sample. Samples were collected from the recirculation line after the wastewater had been thoroughly mixed. Sufficient samples were collected so several series of test could be completed. This allowed evaluation of parameters without changes occurring in the wastewater samples. Two batches of the wastewater were collected for jar testing, since this was the only wastewater available during the test period.

Solutions of ferrous ion and sulfide ion were made to 1,000 mg/L  $\text{Fe}^{+2}$  and  $\text{S}^{-2}$  each, using ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and sodium sulfide monohydrate ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ), respectively. Sulfuric acid (0.2 mL of concentrated) was added to the water prior to the addition of the ferrous sulfate heptahydrate to prevent the formation of ferric ion. Domestic water was used for all solutions. Betz® 1195 Cationic polymer was made to 1000 mg/L using one milliliter of the neat (undiluted) liquid polymer and diluting to 1,000 mL. Betz®1120 Anionic Polymer was made to 100 mg/L using a 0.5 percent sample of the polymer. Sodium hydroxide (5.0 Normal) and Sulfuric Acid (5.25 Normal) were used for pH adjustment. Betz®1160X was made to 1,000 mg/L by weighing out 1 gram of the powder cationic polymer and adding to 1-liter of water. The solution was mixed by shaking for approximately 10 minutes and then shaking periodically for 1 hour. A 1,000 mg/L  $\text{Cr}^{+6}$  solution was made using sodium dichromate ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ). A sample of Duraclean solution from a process tank was used neat for the evaluation of the effect of the addition of the Duraclean to the wastewater.

Initial tests were conducted in order to define the sulfide and ferrous iron concentrations required to reduce the hexavalent chromium to trivalent chromium and achieve metal precipitation. The pH of the solution was adjusted to 7.5 with 5 Normal Sodium Hydroxide Solution. The desired volume of sulfide solution was added to the wastewater. The solution was mixed 2 minutes at 120 RPM. The desired volume of ferrous solution was added. The pH of the

sample was adjusted to 7.2 to 7.5 (the optimum process pH) with 5.25 Normal sulfuric acid after the ferrous addition. The solution was mixed for 2 minutes. The desired volume of the Betz®1195 cationic polymer solution was added and the solution mixed 2 minutes. The desired volume of the Betz® 1120 anionic polymer solution was added and mixing continued at 120 RPM for an additional 2 minutes. The mixing was slowed to 20 RPM. After 2 minutes, mixing was stopped, and the paddles were removed. The solution was allowed to stand 5 minutes and then filtered through a cotton plug. The cotton plug is representative of filtering the treated effluent through a sludge blanket. The sample was analyzed for the desired species. The ferrous concentration was varied at fixed sulfide concentrations.

Polymer requirements was determined at the optimum sulfide and ferrous concentrations. The effects of the polymers were determined through observation of the type of floc formation and settling, as well as, analyzing for the resulting solution turbidity. Solution turbidity was determined both before and after filtering through cotton. Jar testing was conducted in the same manner as described above for determination of the optimum sulfide and ferrous concentration. In the cases, where a cationic or anionic polymer were not added, the mixing was still continued in the same manner as described for their addition.

The effect of increased influent hexavalent chromium concentration was determined by adjusting the wastewater hexavalent chromium to the desired concentration with the sodium dichromate solution. At the higher chromate concentrations (100, 250, and 500 mg/L  $\text{Cr}^{+6}$ ) the powder sodium dichromate was added directly to the wastewater. The pH was adjusted to 7.2 to 7.5 after adjusting the chromate concentration. Jar testing proceeded in the same manner as described above.

The effect of the Duraclean solution was determined by adding the desired volume of the Duraclean solution collected from a process tank to the wastewater prior to adjusting the pH to 7.2 to 7.5. The sulfide and ferrous solutions were added at the optimum concentrations determined above.

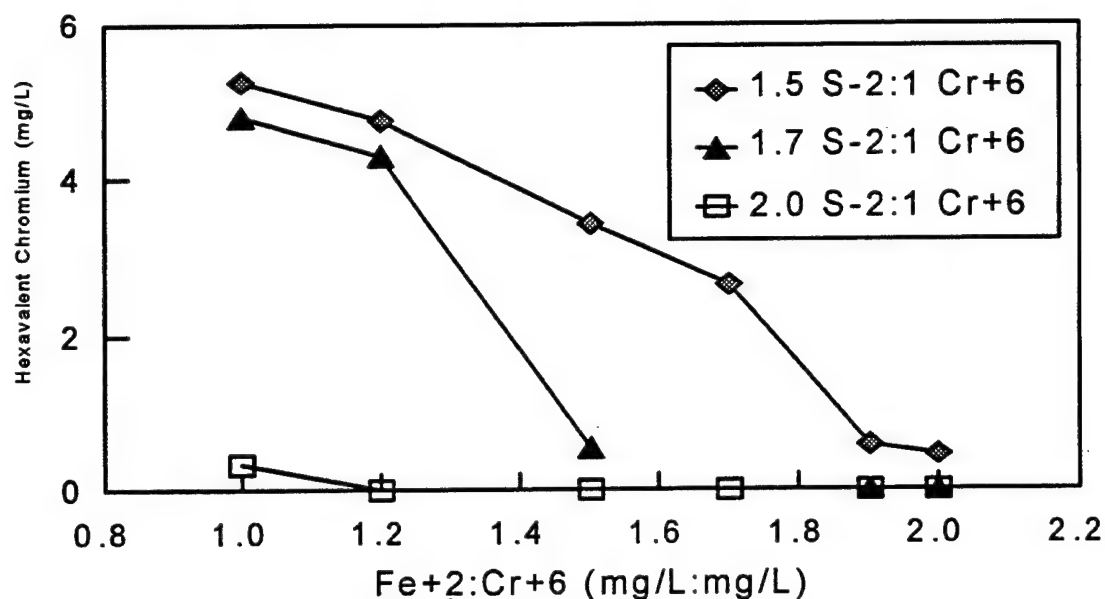
Sludge generation was determined by treating three 1-Liter samples of the industrial wastewater with the Sodium Sulfide/Ferrous Sulfate process at optimum conditions (36 mg/L  $S^{2-}$ , 27 mg/L  $Fe^{+2}$ , 5 mg/L Betz®1195, and 0.5 mg/L Betz®1120). The sludge was collected on a pre-weighed 0.1  $\mu m$  glass fiber filter paper. The filter paper was pre-weighed both wet and dry. The sample was weighed after filtering to determine the wet weight and after drying at low temperature (100°C) overnight to determine the dry weight.

The pH was determined using a Corning 107 pH/temperature meter calibrated with pH 7 and pH 10 buffers. The reacted solution was analyzed for hexavalent chromium using the HACH 1,5-diphenylcarbohydrazide method for hexavalent chromium for water and wastewater and a HACH DR2000 spectrophotometer. Total chromium was determined using the HACH alkaline hypobromite oxidation method. Copper was determined using the HACH Bicinchoninate Method for copper. Iron was determined using the HACH FerroVer Method for total iron. Nickel was determined using the HACH 1-(2-Pyridylazo)-2-Naphthol (PAN) method for nickel. Zinc was determined using the HACH Zincon (2-carboxy-2'-hydroxy-5'sulfoformazyl benzene indicator) Method for zinc. Samples were not acid digested prior to metal analysis. Turbidity was determined using the HACH absorptometric method for turbidity. A sample of the wastewater treated at optimum conditions was submitted to Laucks Testing Laboratories, Inc., Seattle, WA for heavy metal analysis.

### **3.2 RESULTS OF JAR TESTS**

Jar tests were conducted in order to determine the optimum sulfide, ferrous, and cationic and anionic polymers concentrations required to achieve reduction of the hexavalent chromium and removal of the heavy metals to the discharge requirements. The jar test conditions and data are listed in Appendix A.

Figure 4 shows the remaining hexavalent chromium concentration as a function of the ferrous concentrations at fixed sulfide concentrations. The optimum sulfide to ferrous to



**Figure 4 The Hexavalent Chromium Remaining as a Function of the Ferrous Concentration at Fixed Sulfide Concentrations.**

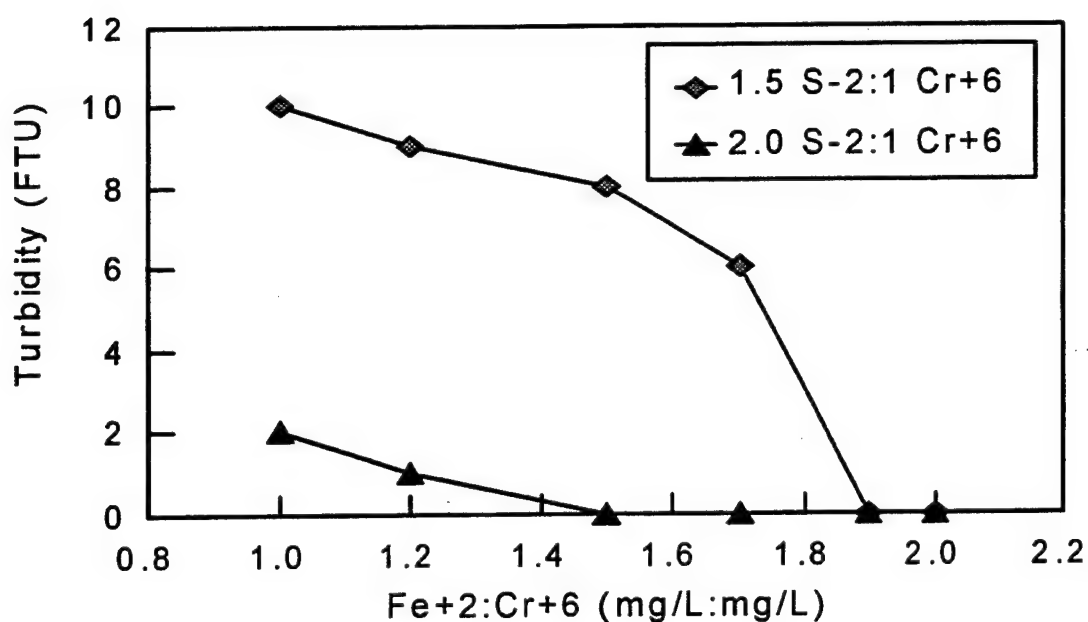
hexavalent chromium ratio was selected at 2 mg/L  $S^{-2}$  per 1.5 mg/L  $Fe^{+2}$  per 1 mg/L  $Cr^{+6}$ . The sulfide concentrations represents a ratio of 1.5, 1.7, and 2 mg/L  $S^{-2}$  to 1 mg/L  $Cr^{+6}$ , with the initial hexavalent chromium concentration being 18 mg/L  $Cr^{+6}$ . Chromium reduction is achieved at 1.7 mg/L  $S^{-2}$  per 1 mg/L  $Cr^{+6}$  and 1.7, 1.9, and 2.0 mg/L  $Fe^{+2}$  per 1 mg/L  $Cr^{+6}$  and at 2 mg/L  $S^{-2}$  per 1 mg/L  $Cr^{+6}$  and 1.5, 1.7, 1.9 and 2.0 mg/L  $Fe^{+2}$  per 1 mg/L  $Cr^{+6}$ . Figure 5 shows the solution turbidity at 1.5 and 2 mg/L  $S^{-2}$  per 1 mg/L  $Cr^{+6}$ . The solution turbidity is near zero at 1.5 mg/L  $S^{-2}$  and 1.9 mg/L  $Fe^{+2}$  per 1 mg/L  $Cr^{+6}$  and 2 mg/L  $S^{-2}$  and 1.5 mg/L  $Fe^{+2}$  per 1 mg/L  $Cr^{+6}$ .

Figures 6 and 7 shows the total chromium and total iron remaining for 2 mg/L  $S^{-2}$  / 1 mg/L  $Cr^{+6}$ .

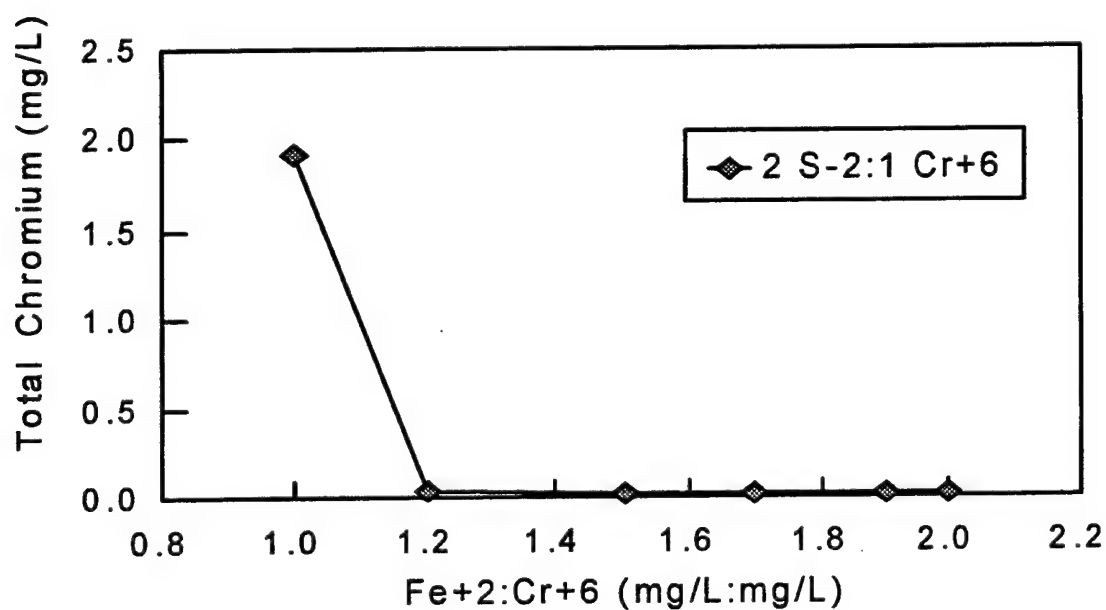
Further testing showed that although chromium reduction could be achieved at the lower concentrations of sulfide and iron, any variations in the solution level in the jars, resulted in hexavalent chromium remaining in the solution. Therefore, the optimum sulfide to ferrous to hexavalent chromium ratio was selected at 2 mg/L  $S^{-2}$  per 1.5 mg/L  $Fe^{+2}$  per 1 mg/L  $Cr^{+6}$ .

Subsequent testing was conducted with the sulfide and ferrous feed at this ratio.

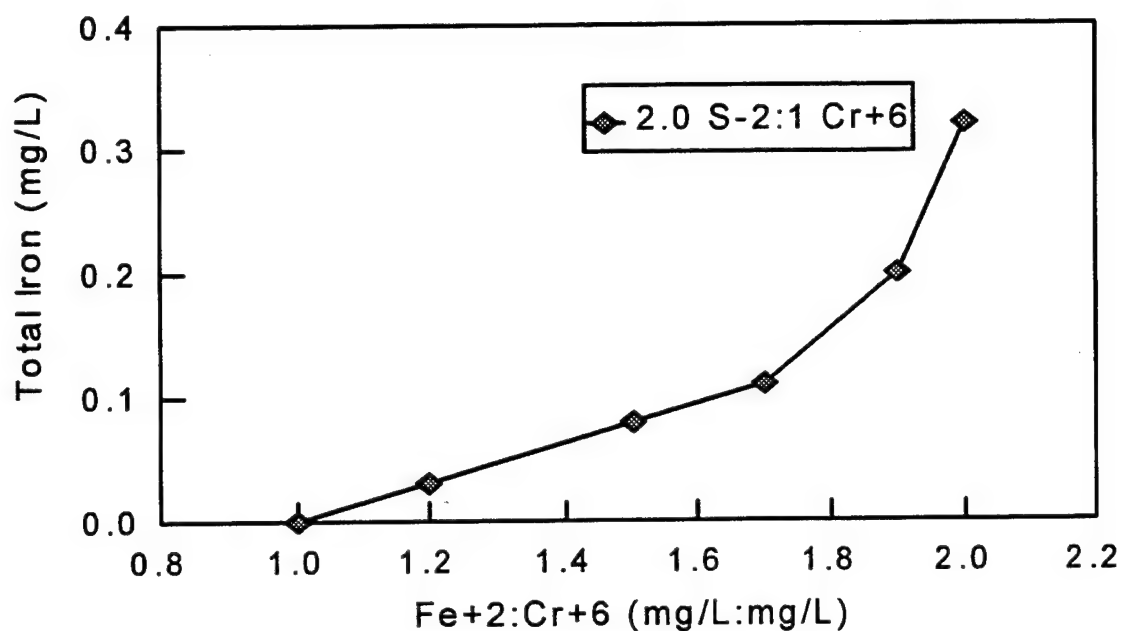
\*\* [ Note that, in Figure 4 and subsequent figures, the notation Fe +2 : Cr+6 (mg/L : mg/L) refers to Fe +2 per Cr+6 (mg/L per mg/L) ]



**Figure 5** The Solution Turbidity as a Function of the Ferrous Concentration at Fixed Sulfide Concentrations.

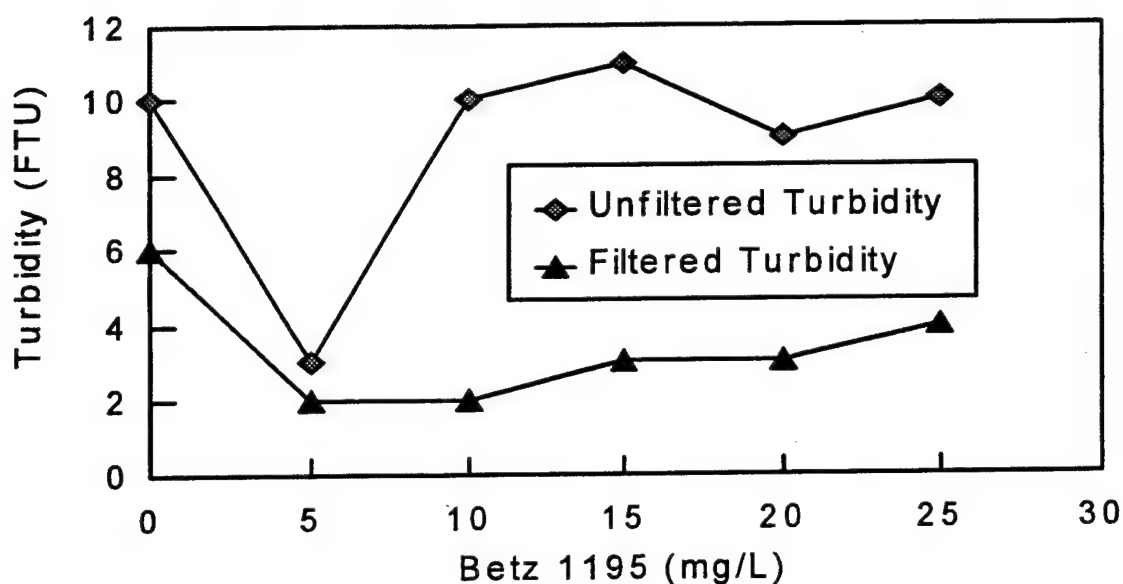


**Figure 6** The Total Chromium Remaining as a Function of the Ferrous Concentration at 36 mg/L Sulfide



**Figure 7** The Total Iron Remaining as a Function of the Ferrous Concentration at 36 mg/L Sulfide.

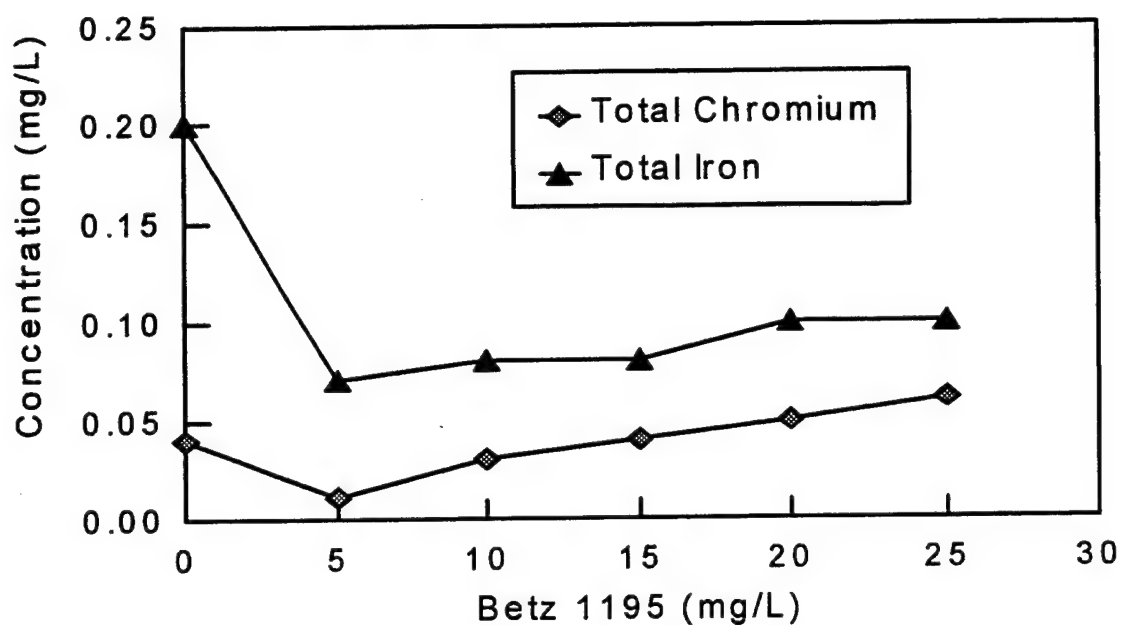
Polymer type and concentration was selected by determining the solution turbidity and total chromium and concentrations as a function of the Betz 1195 concentration with 0.5 mg/L Betz 1120 added, as a function of the Betz®1120 concentration with no cationic polymer added, and as a function of the Betz®1160X cationic polymer concentration with no anionic polymer added. The Betz®1195 cationic polymer was not evaluated without the Betz®1120 addition, because large floc formation did not occur with just the addition of the cationic polymer. Figure 8 shows the turbidity as a function of the Betz®1195 cationic polymer with a fixed concentration of 0.5 mg/L Betz®1120 anionic polymer. The minimum turbidity for both the unfiltered sample and the sample filtered through cotton occurred at 5 mg/L Betz®1195. Figure 9 shows the total chromium and total iron remaining in the treated water. At 5 mg/L Betz®1195 and 0.5 mg/L Betz®1120, the total chromium was 0.01 mg/L while the total iron was 0.07 mg/L.



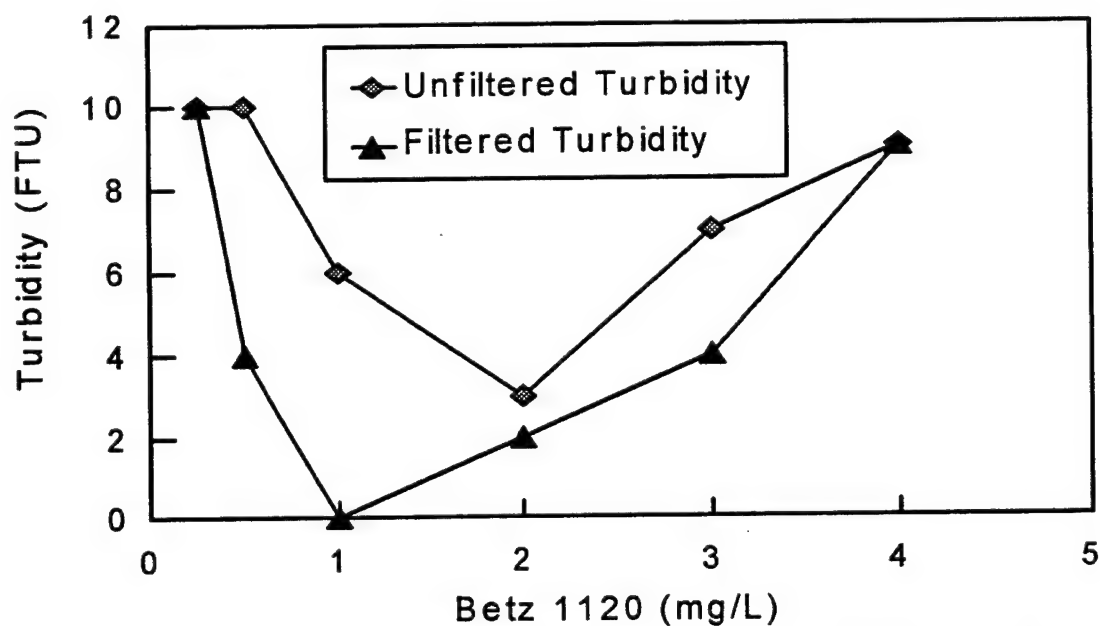
**Figure 8** The Solution Turbidity of the Treated Wastewater as a Function of the Betz®1195 Concentration at Optimum Sulfide and Ferrous Concentrations.

Figure 10 shows the unfiltered and filtered turbidity of the treated wastewater when Betz®1120 was added without the addition of the Betz®1195. The minimum turbidity for the unfiltered sample occurred at 2 mg/L of the Betz®1120, while for the filtered sample the minimum occurred at 1 mg/L Betz®1120. Figure 11 shows the total chromium and total iron remaining in solution. At 1 mg/L Betz®1120, the total iron is below the detection limit of 0.01 mg/L, and the total chromium is 0.03 mg/L. From this test, it appeared that the wastewater could be treated with only the addition of the Betz®1120 anionic polymer at optimum sulfide and ferrous concentrations. However, further testing with only the anionic polymer did not result in solutions of such low turbidities. Apparently, traces of the Betz®1195 cationic polymer remained on the paddle of the jar test apparatus even after washing the paddles and was aiding the clarification. With repeated testing without the addition of the Betz®1195 cationic polymer, the solutions became less clear as the residual polymer was used up. This does indicate, that with the

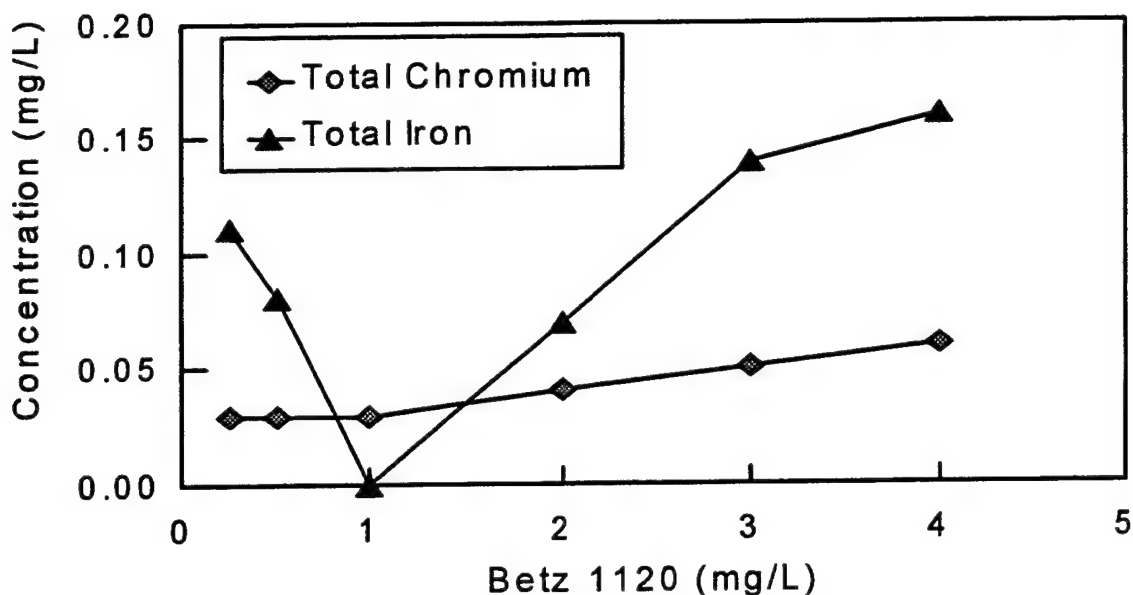




**Figure 9** The Total Chromium and Iron Remaining as a Function of the Betz®1195 Concentration at Optimum Sulfide and Ferrous Concentrations.



**Figure 10** The Solution Turbidity as a Function of the Betz®1120 Concentration at Optimum Sulfide and Ferrous Concentrations.



**Figure 11** The Total Chromium and Iron Remaining as a Function of the Betz®1120 Concentration at Optimum Sulfide and Ferrous Concentrations.

use of a streaming current detector to control the cationic polymer addition, only a minimal concentration of the polymer will be required with the Betz®1120 anionic polymer for settling and clarification of the wastewater at optimum sulfide and ferrous feed concentrations.

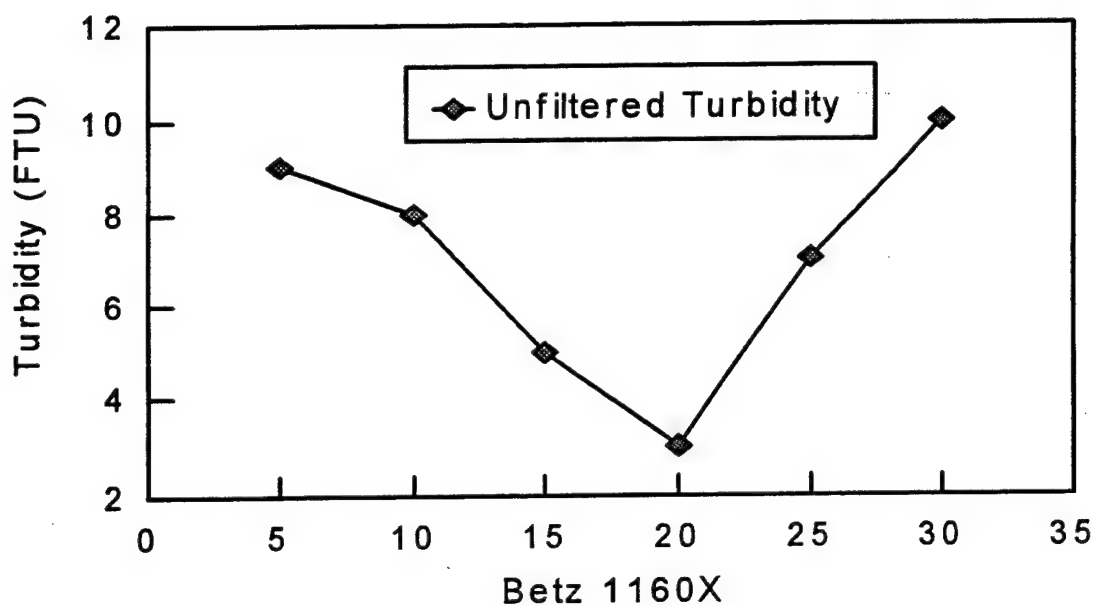
The polymer selection was not tested as a function of the solution pH since extensive laboratory and pilot-scale testing both at Tinker AFB and Pensacola Naval Facility have demonstrated the optimum pH for the SS/FS process to be pH 7.2 to 8.4.

Currently, the Betz®1160X cationic polymer is used with the Sulfuric Acid/Sulfur Dioxide/Caustic process at the NUWC. This polymer was evaluated with the SS/FS process at optimum sulfide and ferrous concentration. Figure 12 shows the unfiltered solution turbidity as a function of the Betz®1160X concentration with no anionic polymer addition. The filtered

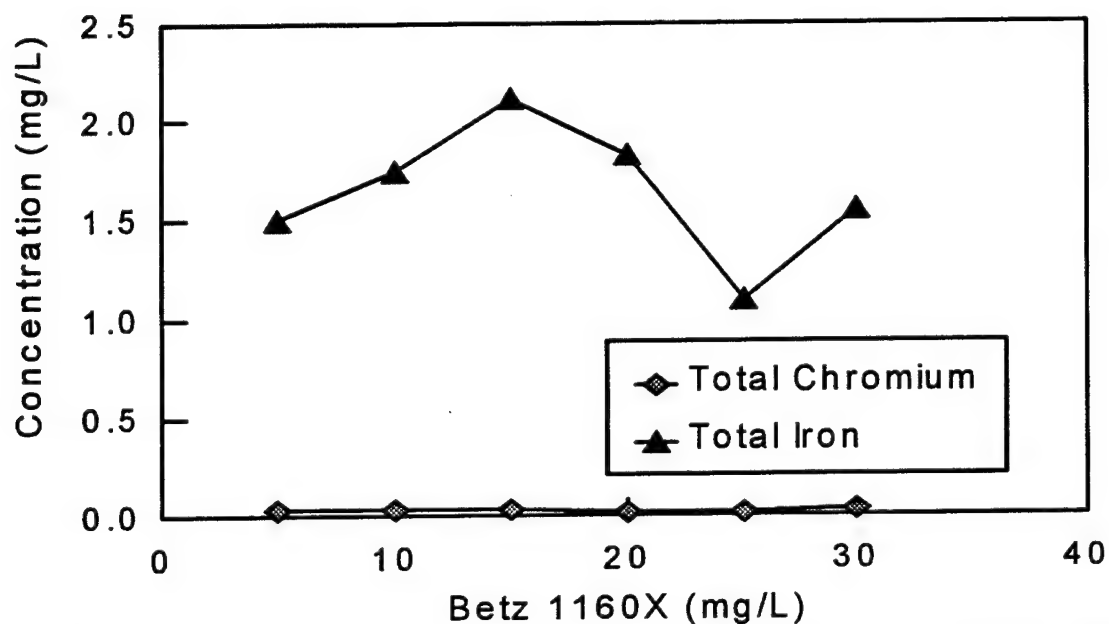
turbidity was zero for the test series. Excellent settling occurred in the treated wastewater and the total chromium was 0.02 to 0.04 mg/L. The total iron remaining in the solution, however, was high as shown in Figure 13. The total iron was greater than 1 mg/L for all concentrations of the Betz®1160X. The optimum pH for chromium reduction and metal precipitation with the SS/FS process is 7.2 to 8.4. The pH for minimum metal solubility with Sulfuric Acid/Sulfur Dioxide/Caustic process is 7.5 to 12 (See Figure 1). The NUWC IWTP operates from pH 8.5 to 9. This would normally be the optimum working pH for the Betz®1160X.

The effect of pH on the SS/FS process was not evaluated as extensive tests have been conducted during process development and implementation at Tinker AFB and process evaluation at the Pensacola to determine the optimum process pH. The optimum process pH is 7.2 to 8.4. Higher pH values result in a fine particulate which is much more difficult to remove even with polymer addition. Additionally, the increased pH results in inefficient chromium reduction.

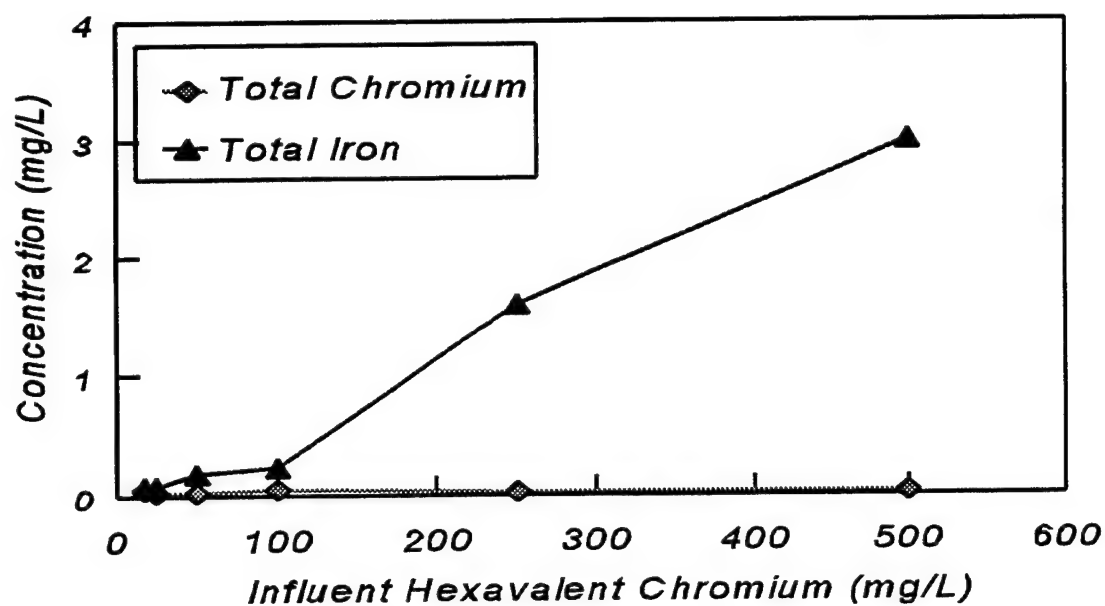
The concentration of the hexavalent chromium in the wastewater during testing was 18 mg/L, while the total chromium concentration was 28 mg/L. The operators felt this was very typical of the wastewater they normally see in the plant. However, during times the chromium may be significantly higher due to spills, floor washings, etc. Therefore, the SS/FS process was evaluated at hexavalent chromium concentrations as high as 500 mg/L  $\text{Cr}^{+6}$ . In the initial test (Figure 14), the sulfide and ferrous was added at 2 mg/L  $\text{S}^{-2}$  per 1.5 mg/L  $\text{Fe}^{+2}$  per 1 mg/L  $\text{Cr}^{+6}$ . The remaining hexavalent chromium concentration in all the tests was below the detection limit of 0.01 mg/L  $\text{Cr}^{+6}$ . The total chromium remained low in all the tests. The iron, however, increased to greater than 3 mg/L as shown in Figure 14. A second series of tests was completed with the sulfide and ferrous at 1 mg/L  $\text{S}^{-2}$  per 1 mg/L  $\text{Fe}^{+2}$  per 1 mg/L  $\text{Cr}^{+6}$ . This would be the normal feed rate at this concentration of hexavalent chromium (i.e. at lower concentrations of  $\text{Cr}^{+6}$ , the feed ratio for the sulfide and ferrous is higher for chromium reduction. As the hexavalent chromium concentration is increased, the sulfide and ferrous feed ratios can be decreased.) The remaining hexavalent chromium was below the detection limit. The total chromium remained low (Fig. 15).



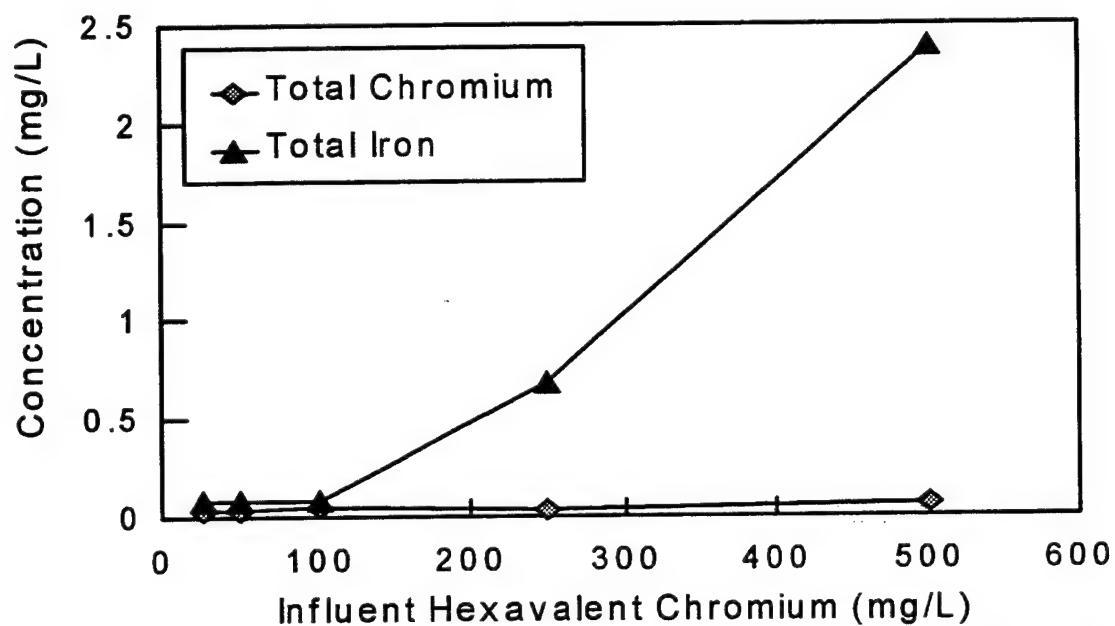
**Figure 12** The Solution Turbidity as a Function of the Betz®1160X Concentration at Optimum Sulfide and Ferrous Concentration.



**Figure 13** The Total Chromium and Iron Remaining in Solution as a Function of the Betz®1160X Concentration at Optimum Sulfide and Ferrous Concentrations.



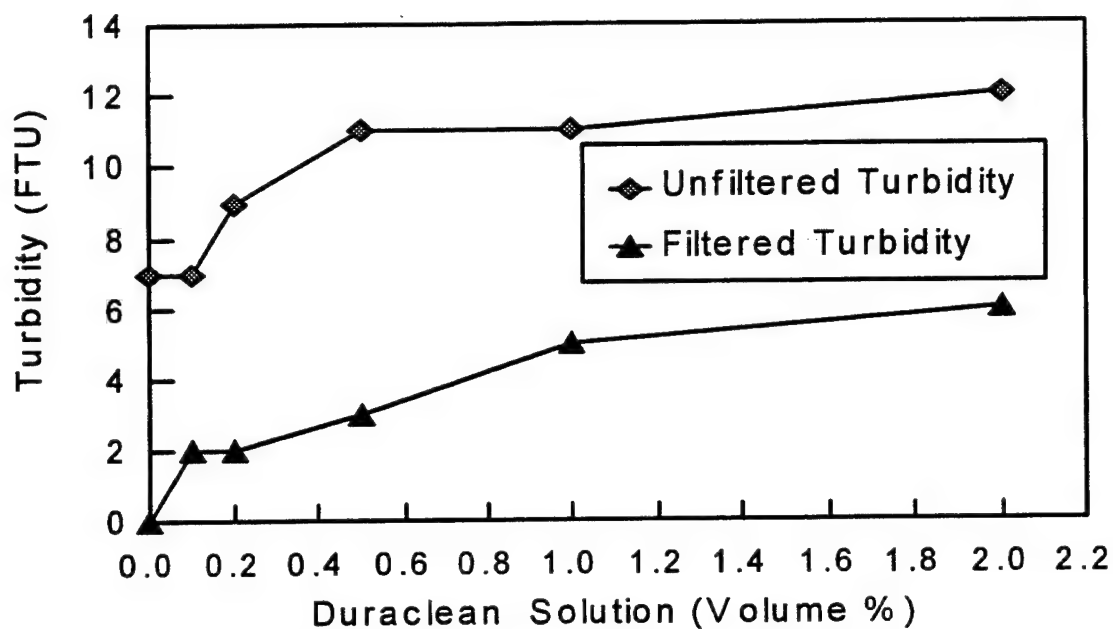
**Figure 14** The Total Chromium and Iron Remaining as a Function of the Chromium concentration at a Feed Ratio of 2 mg/L  $S^{2-}$  per 1.5 mg/L  $Fe^{+2}$  per 1 mg/L  $Cr^{+6}$ .



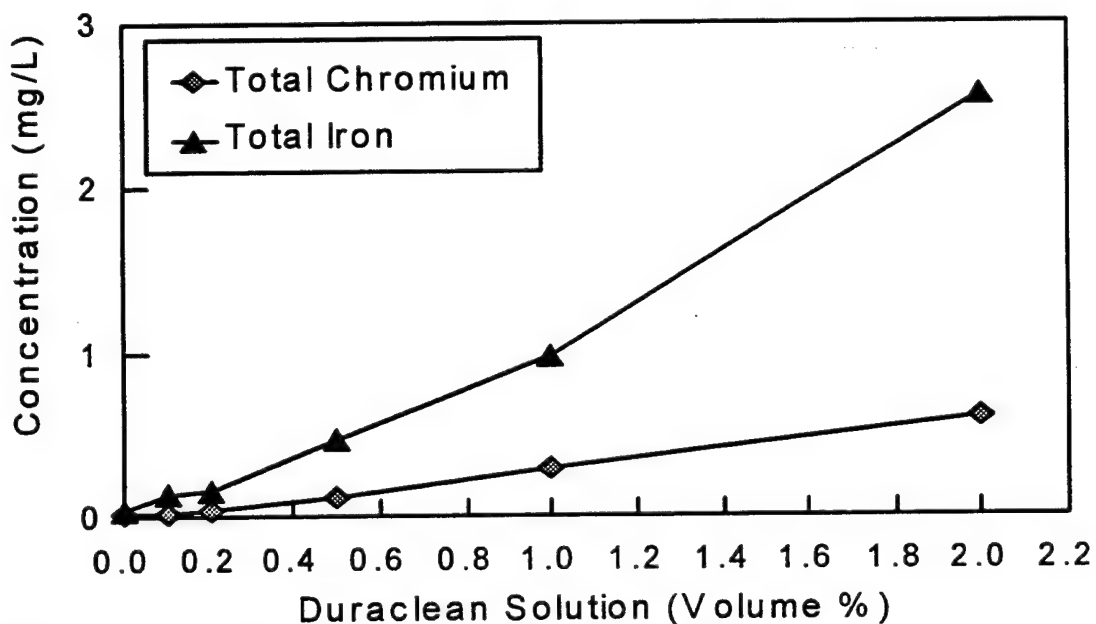
**Figure 15** The Total Chromium and Iron Remaining as a Function of the Chromium Concentration at a Feed Ratio of 1 mg/L  $S^{2-}$  per 1 mg/L  $Fe^{+2}$  per 1 mg/L  $Cr^{+6}$ .

The iron, however, increased to 2.38 mg/L for the test with 500 mg/L  $\text{Cr}^{+6}$ . The Betz®1195 cationic polymer was added at 10 mg/L. Normally as the hexavalent chromium concentration increases, the required cationic polymer concentration increases (Reference 2). In actual plant operation, the cationic polymer concentration would be adjusted to the correct concentration with the streaming current detector and controller. The streaming current detector (SCD) indicates the electrokinetic charge of the water after polymer addition. The polymer is fed so that the charge is maintained slightly positive (two units). Operation with the correct concentration of polymer and filtering the effluent through the sludge bed would reduce the iron concentration in the effluent.

The aqueous cleaner "Duraclean" is used in metal processing at the NUWC. The effect of the addition of a sample of this cleaner on the SS/FS metal precipitation process was evaluated. The cleaner was added at incrementing concentrations to 2 volume percent. The wastewater was then treated with the optimum concentration of sulfide and ferrous (2 mg/L  $\text{S}^{-2}$  per 1.5 mg/L  $\text{Fe}^{+2}$  per 1 mg/L  $\text{Cr}^{+6}$ ). The Betz®1195 cationic polymer was added at 5 mg/L and the Betz®1120 anionic polymer was added at 0.5 mg/L. The effect of the "Duraclean" on the treated wastewater turbidity is shown in Figure 16. The filtered turbidity increased from zero to 7 FTU, while the unfiltered turbidity increased to 12 FTU. The total chromium remaining in the treated wastewater increased to 0.61 mg/L Cr and the total iron to 2.56 mg/L at 2 volume percent of the Duraclean as shown in Figure 17. Two volume percent would represent approximately 720 gallons of the Duraclean cleaning solution in the 36,000 gallon batch. Below 0.5 volume percent, the Duraclean had no effect on the total chromium and only increased the total iron to 0.16 mg/L. Normally, with aqueous cleaners or soaps present, an increase in the concentration of the cationic polymer would be required. This would be controlled in actual plant operation by controlling the cationic polymer addition with the streaming current detector. However, the volume of Duraclean wasted to the plant should be controlled. An impact on the precipitate settleability and clarification is seen when the Duraclean is present with the Sulfuric Acid/Sulfur Dioxide/Caustic treatment process.



**Figure 16** The Solution Turbidity as a Function of the Duraclean Concentration at Optimum Sulfide and Ferrous Concentrations.



**Figure 17** The Total Chromium and Iron Remaining as a Function of the Influent Duraclean Concentration at Optimum Sulfide and Ferrous Concentrations.

The volume of sludge generated from each liter of wastewater was determined. In addition, the treated sample was submitted to Laucks Testing Laboratories, Inc., Seattle, WA for analysis for the heavy metals. The sludge generation is shown in Table 7 for the one liter sample and projected at 50 percent solids for each 10,000 gallons of wastewater treated. The results of the analysis is shown in Table 8. Additionally, a sample of the wastewater treated with the Sulfuric Acid/Sulfur Dioxide/Caustic process in the Industrial Treatment Plant was also submitted for analysis.

It should be noted that the sample treated with the SS/FS process was collected on June 15, 1994, while the sample treated with the Sulfuric Acid/Sulfur Dioxide/Caustic is the effluent for June 21, 1994. The complete analytical report is in Appendix B.

<b>Table 7. Sludge Generation with the Sodium Sulfide/Ferrous Sulfate Metal Precipitation Process.</b>			
Test	Wet Weight* (grams/Liter)	Dried Weight** (grams/Liter)	Sludge Generation*** (lb/10,000 gals wastewater)
1	1.5951	0.3487	58.07
2	1.6697	0.3492	58.15
3	1.3588	0.3753	62.49
Average	1.5412	0.3577	59.56
<p>* The <u>wet weight</u> is the weight of the sludge after filtering.</p> <p>** The <u>dry weight</u> is the weight of the sludge after drying on a hot plate overnight on low heat. This would represent 100 percent solids. Normally, the sludge is approximately 50 percent solids at the Keyport IWTP.</p> <p>*** The <u>sludge generation</u> was projected at 50 percent solids</p>			



**Table 8.**  
**Heavy Metals Concentration of Samples of the Wastewater Treated with the Sulfuric Acid/Sulfur Dioxide/Caustic Process and the Sodium Sulfide/Ferrous Sulfate Process.**

Analyte	Discharge Requirements		Plant Effluent <sup>1</sup> (6/21/94)	SS/FS <sup>2</sup> (6/15/94)
	Daily Maximum	Monthly Average		
Cadmium (mg/L)	1.0	0.5	0.017	0.001 U
Chromium (mg/L)	5.0	2.5	0.12	0.013
Chromium, Hexavalent			0.012	
Copper (mg/L)	4.5	1.8	0.008	0.011
Iron (mg/L)			2.1	0.38
Lead (mg/L)	0.6	0.3	0.005 U	0.005 U
Mercury (mg/L)	0.005	N/A	0.010 U	0.010 U
Nickel (mg/L)	4.1	1.8	0.015	0.020
Silver (mg/L)	2.0	N/A	0.001 U	0.001 U
Sodium (mg/L)			270.	140.
Zinc (mg/L)	4.2	1.8	0.004	0.012

<sup>1</sup> Sample of the plant effluent on June 21, 1994. The sample was treated with the Sulfuric Acid/Sulfur Dioxide/Caustic process in the industrial wastewater treatment plant.

<sup>2</sup> A sample of the influent wastewater collected on June 15, 1994 and treated with the Sodium Sulfide/Ferrous Sulfate process at optimum chemical feed concentrations.

### 3.3 CONCLUSIONS FROM THE JAR TESTS

The application of the Sodium Sulfide/Ferrous Sulfate process to the treatment of the industrial wastewater generated at the NUWC for heavy metal removal was evaluated. The process removed the heavy metals to well below the discharge limits (Table 8). The chemical requirements for the process was determined. These are shown in Table 9.

Evaluation of the polymer requirements indicates that the Betz®1195 cationic polymer will be required with the Betz®1120 anionic polymer for heavy metal removal and solution clarity. The optimum concentration of the Betz®1195 cationic polymer was 5 mg/L or less. A streaming current detector to control the cationic polymer concentration to the process stream can be used to control the polymer feed as the conditions of the wastewater changes.

The hexavalent chromium was reduced and the heavy metals removed at hexavalent chromium concentrations up to 500 mg/L  $\text{Cr}^{+6}$ . At the higher hexavalent chromium concentrations, the chemical feed requirements can be decreased to 1 mg/L  $\text{S}^{-2}$  per 1 mg/L  $\text{Fe}^{+2}$  per 1 mg/L  $\text{Cr}^{+6}$ . An increase in the effluent iron concentration was noted with the increased influent hexavalent chromium concentration. Controlling the polymer with the streaming current detector would reduce the iron concentration in the effluent, as has been shown with previous process testing and implementation.

<p><b>Table 9.</b> <b>The Chemical Feed Requirements for the SS/FS Process to Treat the</b> <b>NUWC IWTP Wastewater.</b></p>	
Sodium Sulfide	2 mg/L $\text{S}^{-2}$ per 1 mg/L $\text{Cr}^{+6}$
Ferrous Sulfate	1.5 mg/L $\text{Fe}^{+2}$ per 1 mg/L $\text{Cr}^{+6}$
Betz®1195 Cationic Polymer	5 mg/L
Betz®1120 Anionic Polymer	0.5 mg/L
pH after ferrous addition	7.2 to 7.8 units

Addition of Duraclean aqueous cleaner solution to the influent of the wastewater did not effect the total chromium removal at concentrations up to 0.5 volume percent. At greater concentrations, there was an increase in the total chromium in the effluent. At 2 volume percent

Duraclean, the total chromium was 0.61 mg/L. This is still much lower than the discharge concentration of 2.5 mg/L Cr. Again, using the streaming current detector to control the polymer feed will reduce the concentration of chromium in the effluent. Additionally, care should be taken to ensure that large volumes of the Duraclean are not fed directly to the plant as the cleaner can seriously reduce the clarification with either the SS/FS process or the Sulfuric Acid/Sulfur Dioxide/Caustic Process.

### **3.4 ESTIMATED PROCESS ECONOMICS**

The chemical usage, sludge generation, and chemical costs with the Sulfuric Acid/Sulfur Dioxide/Caustic process are shown in Table 10 (Reference 20). The annual chemical feed cost for the SS/FS process was projected from the optimum chemical feed requirements. The volume of wastewater used for the calculations was that volume treated from October 1993 through May 1994 plus the average of this volume projected for June, July, August and September of 1994. This volume was 3,141,660 gallons. The estimated costs for the SS/FS process are listed in Table 11. Comparison of the costs for treatment with the SS/FS process with the costs for treatment with the Sulfuric Acid/Sulfur Dioxide/Caustic process shows a potential reduction in the chemical treatment costs of \$3,598/yr or 39 percent. The sludge generation with the SS/FS process is reduced from 30,447 lbs/year to 18,713 lbs/year or by approximately 38.5 percent. At a disposal cost of \$2.786/lb, this represents a \$32,722/yr decrease in the sludge disposal cost. The overall cost savings projected with the implementation of the SS/FS process is \$35,722/year or approximately 38 percent of the chemical and sludge disposal cost with the Sulfuric Acid/Sulfur Dioxide/Caustic process previously being used.

**Table 10.**  
**The Chemical Usage and Sludge Generation with the Current Sulfuric Acid/Sulfur Dioxide/Caustic Process.**

Chemical	Usage	Annual Usage	Annual Cost
50 % Caustic (55 gallon drum) \$148.15/drum	3.5 drums/mo	42 dr/yr	\$ 6,222.00
75 % Sulfuric Acid (55 gallon drum), \$115/drum	1.1 dr/mo	13.2 dr/yr	\$ 1,518.00
Sulfur Dioxide (1 ton cylinder) \$551.80/cylinder	75 lb/wk	3,900 lb/yr	\$ 1,076.00
Betz 1160X (50 lb bag) \$317.16/bag	1 lb/wk	50 lb/yr	\$ 317.00
Total Chemical Feed Requirement			\$ 9,133.00
Sludge Generation (\$2.786/lb)*	586.1 lb/wk	30,447 lb/yr	\$84,825.00
Total Treatment Cost			\$93,960.00

\* Hazardous Waste disposal costs includes disposal, analytical, and tracking costs (Reference 20).

\*\* The Treatment costs includes cyanide, specialty chemicals, and acid/chromium treatment (Reference 20)

Chemical usage and costs are projected from the treatment of 3,141,660 gallons of chromium wastewater from October 1993 through September 1994.

**Table 11.**  
**Projected Chemical Usage and Sludge Generation with**  
**the Sodium Sulfide/Ferrous Sulfate Process**

Chemical	Cost	Annual Usage	Annual Cost
Sulfide Solution (150,000 mg/L S <sup>-2</sup> )	\$0.36/lb	8,806 lb/yr	\$ 3,170.00
Ferrous Sulfate Heptahydrate (FeSO <sub>4</sub> •7H <sub>2</sub> O)	\$0.29/lb if bought as 20 bag lots (50 lb/bag)	3,934 lb/yr	\$ 1,141.00
50 % Caustic	\$148.15/55 gal drum	5.4 dr/yr	\$ 804.00
75 % Sulfuric Acid	\$115/55 gal drum	14.2 gal/yr	\$ 30.00
Betz 1195 Cationic Polymer	\$2.5/lb	130 lb/yr	\$ 325.00
Betz 1120 Anionic Polymer	\$5/lb	13 lb/yr	\$ 65.00
Total Chemical Cost			\$ 5,535.00
Sludge generation (assumes 50% solids).	\$2.786/lb	18,917 lb/yr	\$52,703.00
Total Treatment Cost			\$58,238.00
Cost Savings	38 percent		\$35,722.00
Chemical usage and costs are projected from the treatment of 3,141,660 gallons of chromium wastewater from October 1993 through September 1994.			

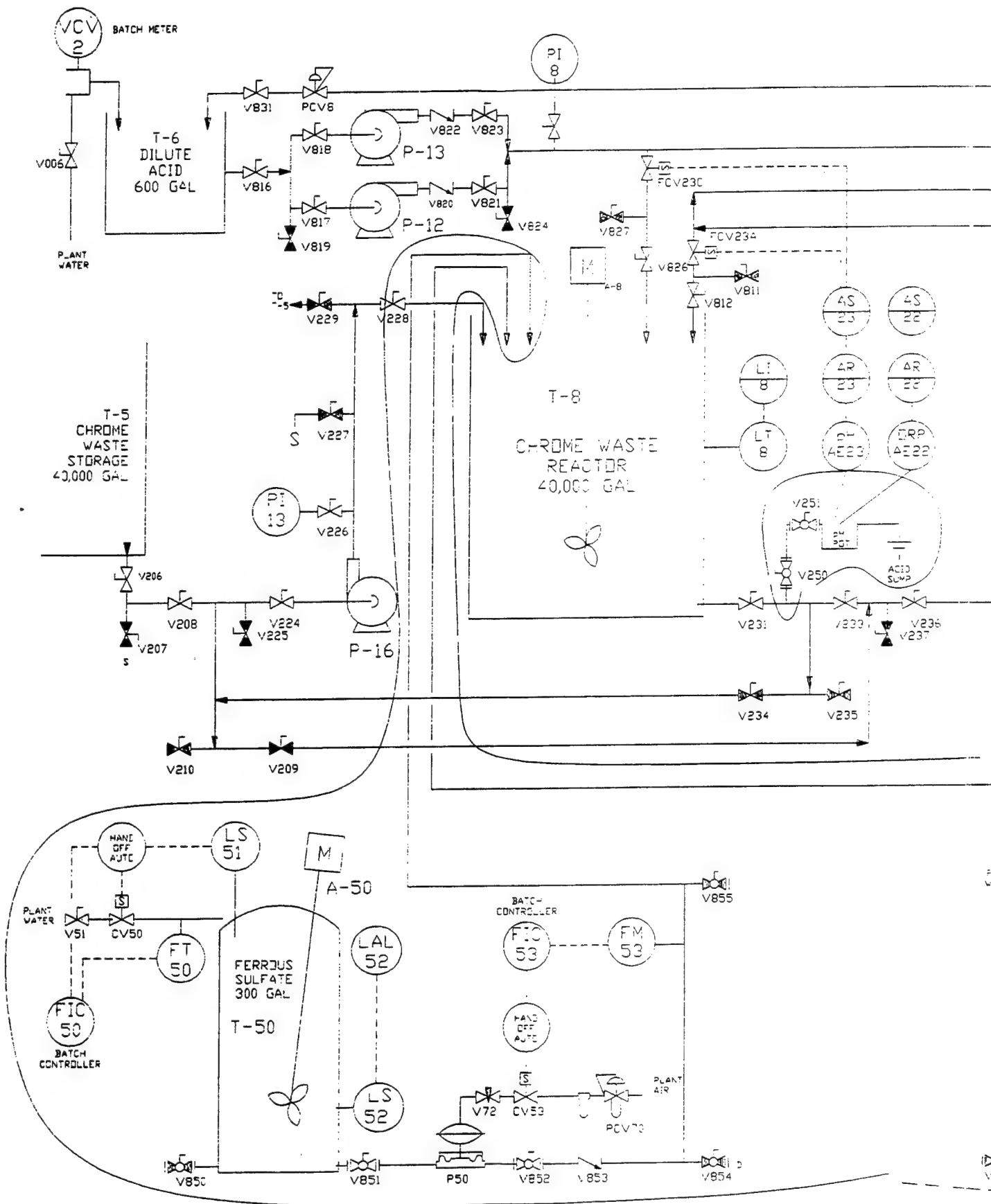
## **4.0 SYSTEM DESIGN AND PLANT MODIFICATIONS**

The existing industrial wastewater treatment plant was reviewed to determine its adaptability to the SS/FS metal precipitation process. The modifications which were required for implementation of the SS/FS process are described below. A SS/FS Process Flow Sketch is shown in Figure 18A and 18B. The diagram includes the required modifications for the SS/FS process. Existing tanks, controls, pumps, and mixers were used with the implementation of the SS/FS process. A streaming current detector and turbidimeter were added for controls. These are also beneficial to the operation of the Sulfuric Acid/Sulfur Dioxide/Caustic process. An additional chemical feed tank and pumps were added for the sodium sulfide and ferrous sulfate.

### **4.1. pH AND OXIDATION REDUCTION POTENTIAL (ORP) IN CHROME REACTOR TANK T-8**

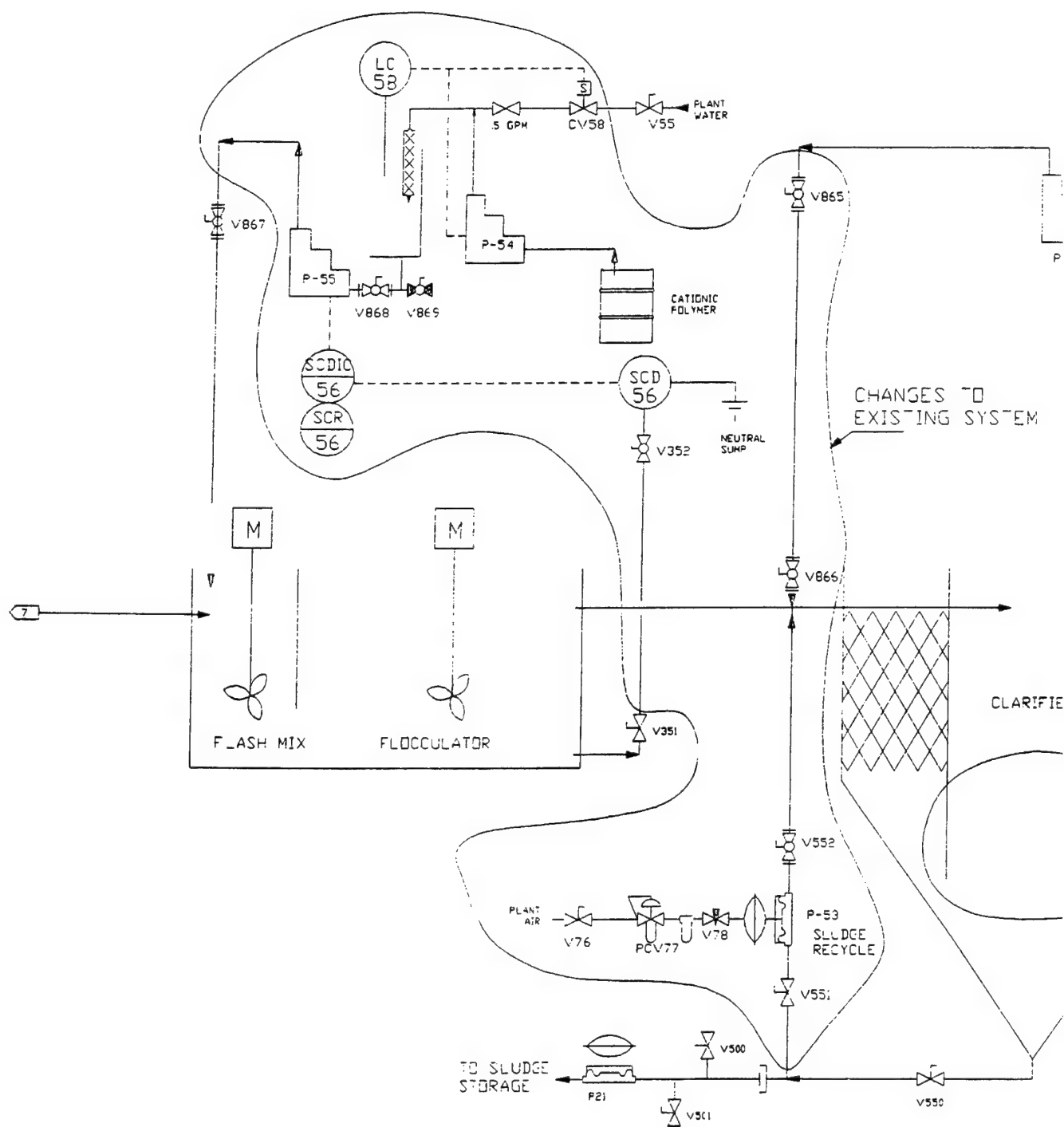
The sample port and pH and ORP transmitters were taken from the Chrome Reaction Tank T-8 outlet pipe next to the tank and connected to the sample pot (a small tank where a continuous sample of wastewater is contained and where the pH and ORP probe are located) located just inside the building with as short a piping run as possible. A new sample pot (Figure 18) was installed to decrease the response time and allow for pH readings when Pump P-2 is not running. Pump P-2 is not required for the SS/FS process.

Controls for auto pH control between pH 7.2 and 7.8 were installed utilizing the existing pH sensor and indicator. A selector switch was used to switch the pH control over to the SS/FS process set points along with ON/OFF timers to control the existing acid and caustic feed valves. The ON/OFF timers allow separate settings for chemical feed time and off time for the reaction and monitoring. The interval timer feeds acid or caustic during the on time and stops it during the off time. This permits mixing and reaction to occur and prevents the feed of excess acid or caustic.









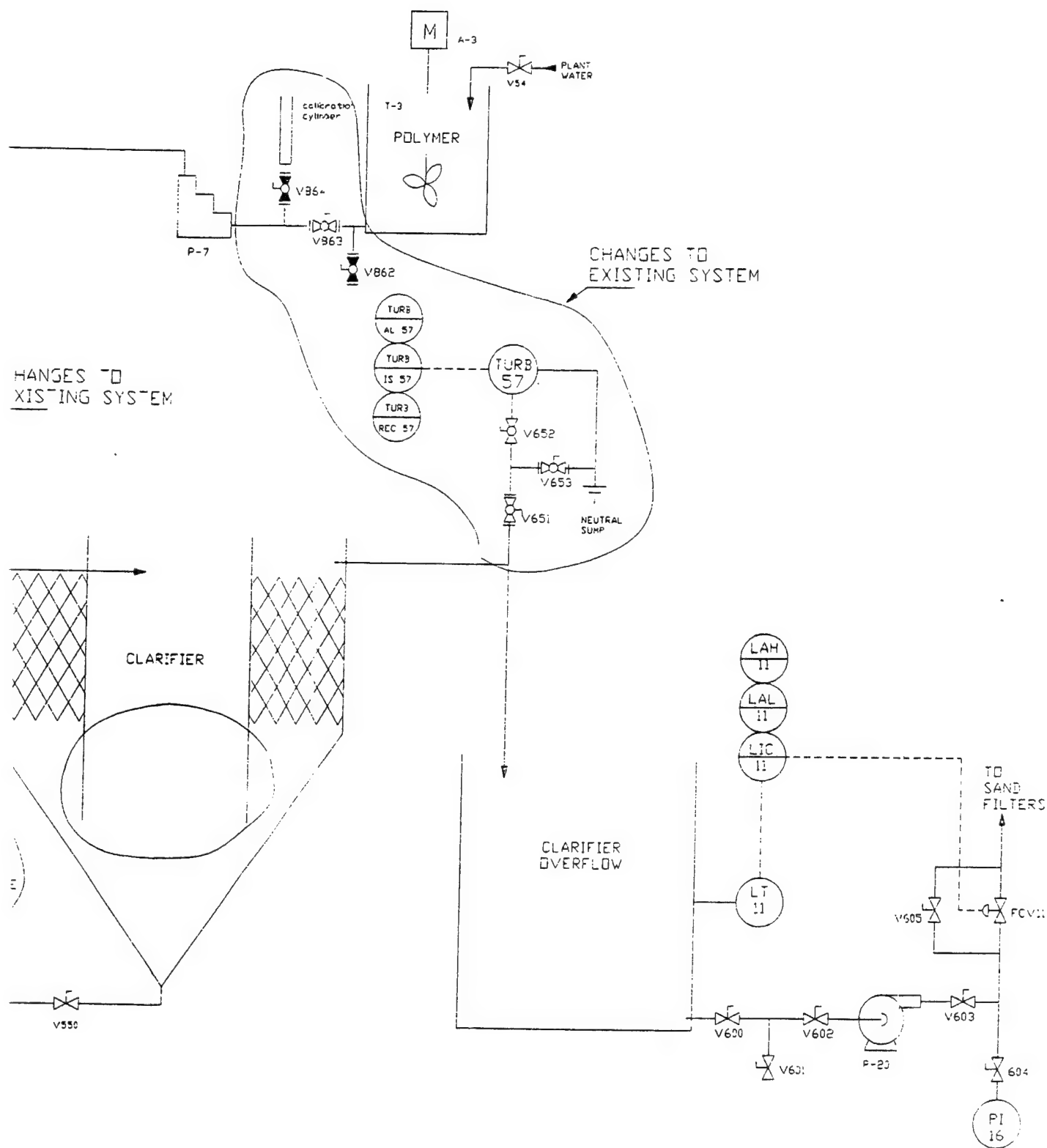


FIGURE 18 B SODIUM SULFIDE/FERROUS SULFATE PROCESS  
FLOW SKETCH  
KEYPORT NUWC INDUSTRIAL WASTE TREATMENT FACILITY

## **4.2 SODIUM SULFIDE FEED SYSTEM**

A system for storage of the sodium sulfide solution and metering the volume of chemical required for the volume of wastewater and metal concentration was installed. A 300 gallon polyethylene tank set in the neutral sump equipment trench receives drummed liquid sodium sulfide solution. The chemical is metered from this tank to the Chrome Reaction tank by an air driven diaphragm pump. The volume to be metered is determined by the operator and set into a batch controller with a manual start for the chemical feed. Manual feed is also possible.

## **4.3 FERROUS SULFATE FEED SYSTEM**

The ferrous sulfate solution is made up from dry bagged chemical in a 300 gallon tank. The make up system consists of a bench and chemical feed funnel to feed chemical into the tank and a batch controller to set the amount of water necessary to make the desired concentration of feed stock. The funnel directs the powder chemical into the feed tank and helps protect the operator from the dust and powder. The ferrous sulfate is metered from this tank to the Chrome Reaction Tank by an air driven diaphragm pump. The volume to be metered is determined by the operator and set into a batch controller with a manual start of the chemical feed. Manual feed is also possible.

## **4.4 CATIONIC POLYMER FEED AND CONTROL SYSTEM**

Cationic polymer is metered into the flocculator from bulk drums by a polymer dilution/injection system. Polymer feed rate is controlled by a streaming current instrument consisting of a sensor, indicator/controller and recorder. The streaming current detector takes a sample flow from the flocculator, determines the streaming potential, and controls the feed rate of the polymer pump to achieve the desired streaming potential. This instrument is housed in a control panel with the sodium sulfide and ferrous sulfate feed controls next to the ferrous sulfate

storage tank. The sensor unit is located by the door to the flocculator tank area. The polymer pump can also be controlled manually.

#### **4.5 TURBIDITY MONITOR**

A Rosemont turbidity monitoring instrument was installed to monitor the clarifier effluent turbidity. It is displayed on the SS/FS control panel and recorded with the streaming current. The sample gravity flows continuously from the clarifier outlet pipe to the sensor mounted at the end of the cyanide treatment equipment tunnel with the spent sample flowing to the neutral sump (the sump which receives the non-acidic or caustic waste).

#### **4.6 SLUDGE RECIRCULATION**

Sludge from the bottom of the clarifier is recirculated to the inlet of the clarifier to aid in the solids contacting and building of denser floc particles. An air driven diaphragm pump was installed at the base of the clarifier to draw sludge from the existing sludge line and discharge it into the clarifier inlet pipe next to the clarifier. Flow is manually controlled from 0 to 35 gpm.

#### **4.7 CLARIFIER WELL**

The skirt of the center well of the clarifier well was extended 20 inches deeper. Extending the well allows the effluent to flow through the sludge blanket, thereby, allowing the sludge blanket to serve as a filter to remove fines in the treated wastewater.

## 5.0 PLANT OPERATION

The NUWC IWTP was operated with chemical usage and sludge generation data collected using the Sulfuric Acid/Sulfur Dioxide/Caustic chromium reduction metal precipitation process. Table 12 shows the influent analysis for the Chrome Reactor Wastewater during that time period.

The SS/FS process was then implemented at the NUWC IWTP. The sodium sulfide solution was transferred to the sulfide feed tank. Two fifty-five gallon drums of the solution having 150,000 mg/L  $S^{2-}$  was ordered. The solution had crystallized due to low temperatures after being received on base. It is recommended that liquid sodium sulfide should not be stored below 52°F to avoid crystallization. As much of the crystalline sulfide as possible was transferred to the feed tank and dissolved. Final analysis of the solution in the feed tank showed the concentration to be 100,000 mg/L  $S^{2-}$ . The ferrous solution was made up using six 50-pounds bag of ferrous sulfate heptahydrate in 110 gallons of plant water to which 480 mL of concentrated sulfuric acid was added. The ferrous sulfate bags were wet and possibly the chemical was slightly oxidized as a result. When made up, the solution appeared to be more ferric iron than ferrous iron.

The process was started up on April 3, 1995. Approximately 26,000 gallons of wastewater having a hexavalent chromium concentration of 15 mg/L was treated for chromium reduction. The 15 mg/L  $Cr^{+6}$  was due to the addition of approximately 25 gallons of alodining solution to the wastewater. Treatment required approximately 13 gallons of the sulfide solution and 8 gallons of the ferrous solution. Initial treatment resulted in chromium reduction to approximately 0.03 mg/L  $Cr^{+6}$ . An additional 3 gallons of the sulfide solution and 2 gallons of the ferrous solution resulted in chromium reduction to less than detection. It was noted that during these evaluations, the method generally used by NUWC plant personnel showed no hexavalent chromium remaining when the HACH method showed the 0.03 mg/L  $Cr^{+6}$ . After the additional sulfide and ferrous addition, the HACH method showed no hexavalent chromium. The entire chromium treatment period took approximately 30 to 45 minutes in contrast to 4 to 5 hours

<p align="center"><b>Table 12.</b> <b>NUWC IWTP Chrome Reactor Wastewater Analysis</b></p>					
Constituent	3/14/95	3/17/95	3/20/95	3/28/95	3/29/95
Chromium (mg/L)	4	30	37	27	19
Nickel (mg/L)	5	9	7	<1	<1
Cadmium (mg/L)	<1	<1	<1	<1	<1
Lead (mg/L)	1	<1	<1	<1	<1
Zinc (mg/L)	<1	1	1	1	<1
Copper (mg/L)	<1	<1	<1	<1	<1
Silver (mg/L)	<1	<1	<1	<1	<1
Antimony (mg/L)	<1	<1	<1	<1	<1
Beryllium (mg/L)	<1	<1	<1	<1	<1
Arsenic (mg/L)	<1	<1	3	<1	<1
Selenium (mg/L)	<1	<1	<1	<1	<1
Thallium (mg/L)	<1	<1	<1	<1	<1

reaction period required with the Sulfuric Acid/Sulfur Dioxide/Caustic treatment process. This includes the time to pump the chemicals, adjust the pH, and reduce the chromium.

Sludge recirculation was started in the clarifier to fluff the sludge bed. Because, little change had occurred in the bed, Betz®1120 anionic polymer feed was started to the clarifier at 0.5 mg/L on the morning of April 5, 1995. The Betz®1195 cationic polymer was made up. The polymer was pumped to fill the line to the flocculator. Flow of the treated wastewater from the Intermediate Storage Tank was initiated. The streaming current detector was placed in the AUTO position to control the cationic polymer feed. Due to the presence of the Betz®1160X in the flocculator, the initial streaming current of the wastewater was approximately 5 units. As operation, progressed, the streaming current decreased to -0.16 units. At this time, the streaming

current controller was set to control the Betz®1195 cationic polymer feed. However, the controller would control from 100 percent to 0 percent of the pump rate. The controller was therefore placed into manual so that the polymer flow rate and requirement could be controlled and determined. The flow requirement was approximate 12 percent of the speed with the pump strokes decreased to 50 percent.

During initial start up of the flow to the flocculator and clarifier, there was some solids carryover from one side of the clarifier. It is believed this is due partially from start up from no flow to 40 gpm flow and from the mixing of the two solutions at pH 8.6 and 7.5. The anionic polymer feed was increased slightly to accommodate this (0.5 mg/L to 0.75 mg/L). During this period the turbidity increased to approximately 6.8 NTU.

After operation for approximately 2 hours, the effluent Turbidity was 3.6 NTU. During the remainder of the day, the effluent turbidity remained at this low value, except when the streaming current dropped to a negative value for approximate an hour. The turbidity, then increased to 4.6. With adjustment of the cationic polymer feed, the turbidity returned to 3.0 NTU.

## **5.1 COMMENTS ON THE INITIAL START UP OF THE SS/FS PROCESS**

The initial process start up and operation of the SS/FS process at the NUWC, Keyport, WA, identified some problems that resulted in having to shut down the process about one month later. The following observations, comments from the plant operators and the plant chemist/ environmental engineer, and attempted corrective actions are given as a narrative of this period:

- During the process initial start-up (April 4, 1995), the chromium reduction reaction proceeded rapidly. Within 30 minutes of start up the wastewater had been processed and was ready to be transferred to the Intermediate Storage Tank. Some additional chemical was required, (approximately 3 gallons each of the

Sodium sulfide and the ferrous sulfate solutions) than estimated in the Tables provided with the Operations and Maintenance (O&M) Manual. Since, all wastewater volumes are estimated, this was not a concern.

- During the first and second weeks of operation, chromium reduction and heavy metal precipitation proceeded as was normal with the SS/FS process. The treated wastewater was clarified with no “pin floc” or particulate carryover. In fact, the operators noted the lack of sludge buildup as they did not have to waste sludge, i.e. pump sludge from the bottom of the clarifier.
- After approximately 2 weeks of operation, the operators noted that the chromium reduction did not occur as rapidly as it had initially, but would occur if additional chemicals were added or the wastewater was allowed to sit for several hours after the addition of the SS/FS. During this same time they also noted a decrease in the clarification, (i.e. It was difficult to control the sludge bed level). This is indicative of a decrease in the effectiveness of the ferrous sulfate as a catalyst in the chromium reduction. During initial make up of the ferrous sulfate solution, it was noted that the bags of the chemicals got wet during shipment. In addition, the ferrous sulfate powder was not the normal green ferrous iron color. This may be partially due to getting wet, but also indicated a poor initial quality of the chemical. When the ferrous sulfate solution was made up according to the standard procedure of adding 200 mL concentrated sulfuric acid per 50 gallons of water and then adding the ferrous sulfate, the solution was a rust brown instead of the clear green color normally seen.
- It was recommended that a new solution of the ferrous sulfate be made up. During pilot testing of the process at the Public Works Center, Pensacola, it had been noted that when the ferrous solution had become ferric, good clarification did not



occur even though the chromium could be reduced. Replacing the solution with fresh ferrous solution, resulted in immediate correction of this problem.

- In addition, it was recommended that ferrous sulfate powder be added to the intermediate storage tank and the flocculator (approximately one pound each) to aid the clarification on the batch that had been previously processed and was causing difficulty in the clarification. The operators noted that this seemed to help the process.
- During the week of May 1, 1995, conversations with the operator indicated that there were problems with the clarification. However fresh ferrous solution had not been made up because the plant was running low on the sulfide solution and a source for the sulfide solution had not been found. The plant personnel, therefore, did not want to proceed with the make up of the ferrous solution. Several sources for the sulfide solution were identified and additional sulfide solutions were obtained.
- New ferrous solution was made up. The solution was the green color indicating the iron was ferrous and not ferric. The reaction time went back to the original rapid reaction expected with the process. However, operational problems were still noted as follows:
  - It was very difficult to handle the sludge bed. The sludge was buoyed up near the top of the settling cones.
  - Pin floc was carried over the clarifier in significant quantity.
  - Changes in polymer concentration did not ease any of the operational problems.
  - The solution in the chrome reactor after addition of the sulfide and ferrous solutions and pH adjustment is a dark black brown color. This is what one would expect to see with the SS/FS process at the concentration of

chromium present in the wastewater. After pumping the solution to the intermediate tank, and mixing during the day and over night the solution turns a red brown color.

- pH in the intermediate tank decreased to less than 7 with the mixing, requiring pH adjustment in this tank with caustic before clarification the next morning. Additionally the pH had to be checked and adjusted throughout the day. In order to achieve clarification, the pH had to be in the range of 7.5 to 7.6.
- During initial start up, the sludge in the clarifier went from the light color seen with the hydroxide precipitation color to the darker black brown color seen with the SS/FS process. However with further operation, the sludge color was returning to the lighter color.

Due to these difficulties, the process was shut down, and chromium reduction metal precipitation returned to the Sulfuric Acid/Sulfur Dioxide/Caustic Process pending an understanding of the problem and proposed resolution.

## **5.2 LESSONS LEARNED**

The SS/FS process has been demonstrated in continuous operation and on a small scale in batch operations. The industrial wastewater treatment process at the NUWC Keyport, while being a batch operation, has several steps that are not normally present in batch processes. During normal batch operation, the chromium reduction and heavy metal precipitation occurs in one tank. The metals may be removed by settling in this tank or transferring to a clarifier. The polymers are either added with the transfer or in the settling tank. At the NUWC IWTP, the solution is transferred after chromium reduction to the intermediate storage tank where it is held over night or may be held over a weekend. The mixer in the tank causes a great deal of solution aeration. Because of the presence of the precipitated heavy metals, the solution must be mixed to

prevent settling. The mixer impeller reaches a depth in the intermediate storage tank that leaves about 20% of the tank volume below the level of the impeller.

It is believed that the aeration and holding in the intermediate storage tank is converting the iron to the ferric form and oxidizing the sulfide to sulfate. The decrease in pH is indicative of such a reaction occurring. Precipitation at 7.5 to 7.6 is a very low pH for hydroxide precipitation. Since the polymers were selected based on the precipitation with the SS/FS process, they were not as effective at this pH with the hydroxide precipitation. In effect, the SS/FS process was only being used at Keyport to reduce the chromium, while metal precipitation was by hydroxide precipitation. Since approximately 20 percent of the volume remained in the intermediate tank, time was required to replace the process solution. The higher pH of the remaining solution slowed the sulfide oxidation. Additionally, the higher pH in the sludge (which may have been as high as pH 12) help precipitate the heavy metals and enhanced the sludge settling. As the solutions and sludge were replaced with low pH solutions, then the problem became more pronounced. Thus, under the then existing method of operating the IWTP at Keyport, ideal SS/FS operation was not achieved.

In order to achieve true SS/FS process demonstration, several steps in the operating procedure were suggested and these are outlined below:

- In order to operate the SS/FS process in the batch mode for the NUWC facility, it was decided that only wastewater which could be processed during one days operation would be treated for chromium reduction. This allowed processing through the intermediate storage tank without holding the treated wastewater overnight, thus eliminating potential oxidation.
- It was suggested that as much wastewater be sent from the intermediate storage tank to the clarifier that could be processed in one day in the clarifier.

- If wastewater remained in the intermediate storage tank by day's end, the mixer impeller would be turned off and kept off overnight to avoid aeration and oxidation of the iron and sulfide.
- The sludge recirculation rate was increased so as to buoy up the sludge more in the clarifier. In this manner the sludge bed could better serve as a filter for the pin floc and eliminate floc carryover.

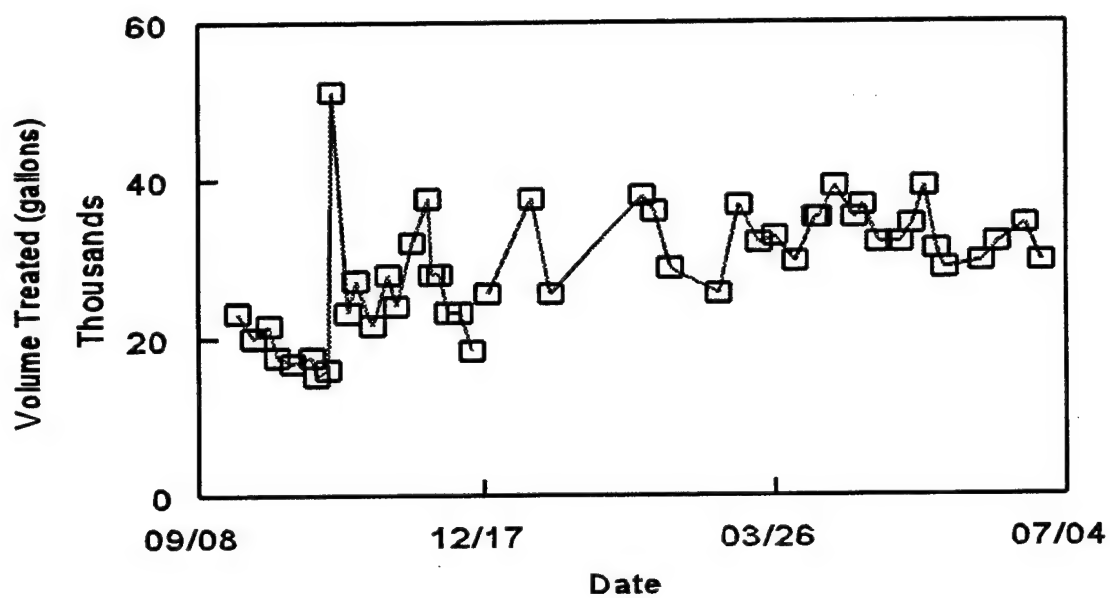
### 5.3 SS/FS PROCESS OPERATION

The SS/FS Process was restarted in the manner suggested above. New chemicals were purchased and solutions prepared. Initially, batch wastewater volumes were kept small. One of the polymer pumps that indicated low flows was recalibrated. The sludge recirculation rate was increased. The cationic polymer use was switched back to the original Betz® 1160 X in March 1996. The recirculation pump was turned off.

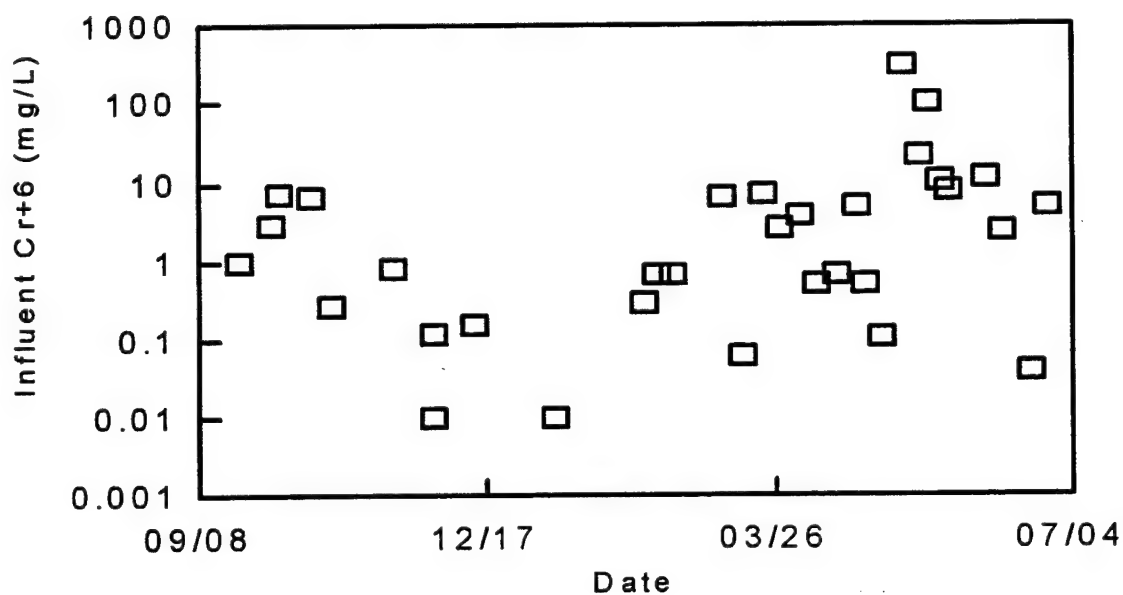
Table 13 summarizes the influent wastewater data and SS/FS chemical additions during this operational period. Figure 19 is a graph of the volume of water treated during this period. Figures 20 and 21 shows the influent hexavalent chromium concentration and pH of the wastewater. Figures 22 and 23 shows the sulfide and ferrous usage during this same time period. Appendix C and D show the operating data for this time period. As can see from Figure 20, the influent  $\text{Cr}^{+6}$  concentration was high in September and then maintained at a low concentration to compare the process with operation of the  $\text{H}_2\text{SO}_4/\text{SO}_2$ /Caustic process operated under similar conditions. During the February and March operation of the process, the influent hexavalent chromium concentration was increased by adding spent high concentration chromium solution to the influent wastewater tank. Throughout the operation, the influent pH varied from 2 to 12 as shown in Figure 21.

Table 13. Summary of the Influent Data for the Sodium Sulfide/ Ferrous Sulfate Process at the NUWC IWTP.					
Date	Volume gal.	Influent pH	Cr+6 mg/L	Sodium Sulfide gal.added	Ferrous Sulfate gal.added
9/22/95	23,200	6.8	1.00	2.4	5.4
9/28/95	20,000	1.9			
10/3/95	21,600	6.0	3.00	1.5	4.7
10/6/95	17,600	6.3	7.00	2.7	6.1
10/11/95	17,000	6.0	0.00	1.2	2.2
10/18/95	17,600	7.0	6.50	2.7	5.6
10/20/95	15,040	2.6	0.00	1.0	2.0
10/24/95	16,000	6.0	0.26	1.1	2.0
10/25/95	21,200	6.1	0.00	1.0	1.9
10/31/95	23,200	10.2	0.00	1.6	3.2
11/3/95	27,200	5.8	0.00	1.8	3.4
11/8/95	21,600	7.6	0.00	1.5	3.0
11/14/95	28,000	7.5	0.84	1.9	3.8
11/17/95	24,000	2.1	0.00	1.6	3.3
11/22/95	32,000	5.0	0.00	2.2	4.0
11/28/95	37,600	2.6	0.12	2.9	5.0
11/29/95	28,000	2.8	0.01	1.9	3.8
12/1/95	28,000	2.4	0.00	1.9	3.8
12/5/95	23,200	3.8	0.00	1.6	3.2
12/8/95	23,200	7.5	0.00	1.6	3.2
12/12/95	18,400	7.1	0.15	1.2	2.6
12/14/95	21,600	1.8	0.00	1.5	3.8
12/18/95	25,600	9.6	0.00	1.7	3.5
1/2/96	37,600	7.2	0.00	2.6	5.0
1/9/96	25,600	5.6	0.01	1.7	3.2
2/10/96	38,200	11.6	0.30	2.7	5.2
2/14/96	36,000	9.2	0.66	4.9	9.3
2/20/96	28,800	12.1	0.66	2.4	4.6
3/7/96	25,600	3.1	6.60	11.8	21.4
3/14/96	36,800	5.2	0.06	2.5	4.6

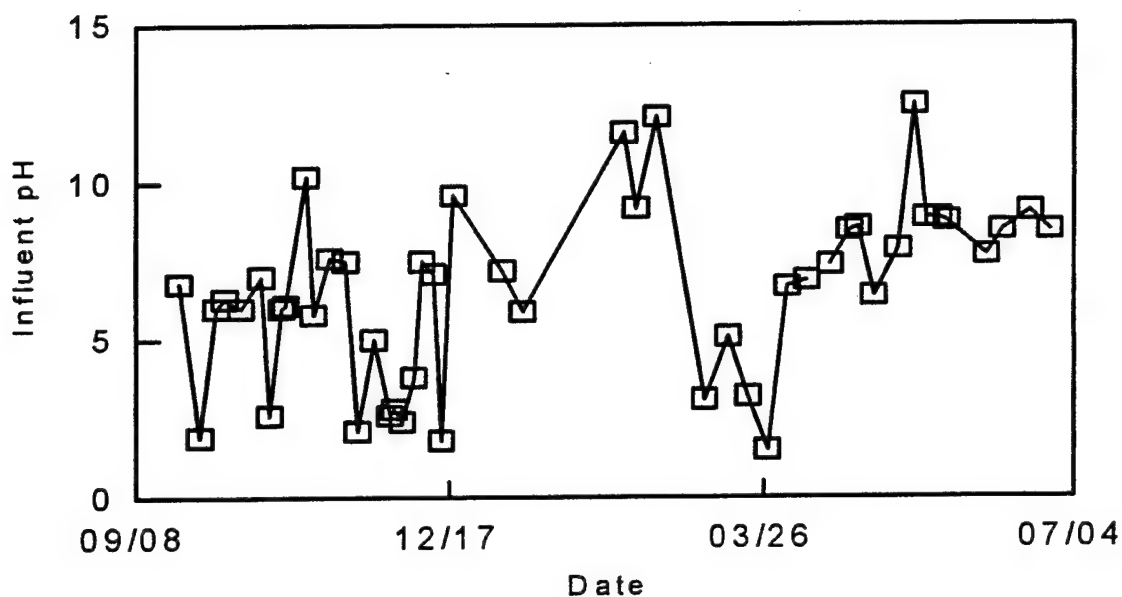
Table 13. Summary of the Influent Data for the Sodium Sulfide/ Ferrous Sulfate Process at the NUWC IWTP.					
3/21/96	32,000	3.2	7.00	5.8	11.2
3/27/96	32,800	1.5	2.60	3.9	7.7
4/3/96	29,600	6.7	3.90	2.6	4.0
4/9/96	35,200	6.9	0.52	2.5	4.5
4/16/96	39,200	7.4	0.66	2.7	5.0
4/23/96	35,200	8.5	5.20	2.5	5.3
4/26/96	36,800	8.6	0.51	6.5	7.0
5/1/96	32,000	6.4	0.11	2.2	4.0
5/8/96	32,000	7.9	310.00	89.6	133.0
5/13/96	34,400	12.5	21.00	6.0	8.3
5/17/96	39,200	8.9	100.00	26.1	49.0
5/21/96	31,200	8.9	11.00	12.4	16.6
5/24/96	28,800	8.8	8.00	5.2	9.0
6/5/96	29,600	7.7	12.00	12.9	20.0
6/11/96	32,000	8.5	2.40	2.2	4.4
6/20/96	34,400	9.1	0.04	8.5	13.0
6/26/96	29,600	8.5	5.00	5.0	10.0
Total	1,323,400			263.7	357.1
Average	28,157	6.6	11.00	5.6	7.6
Minimum	15,000	1.5	0.00	1.0	1.9
Maximum	39,200	12.5	310.00	89.6	133.0



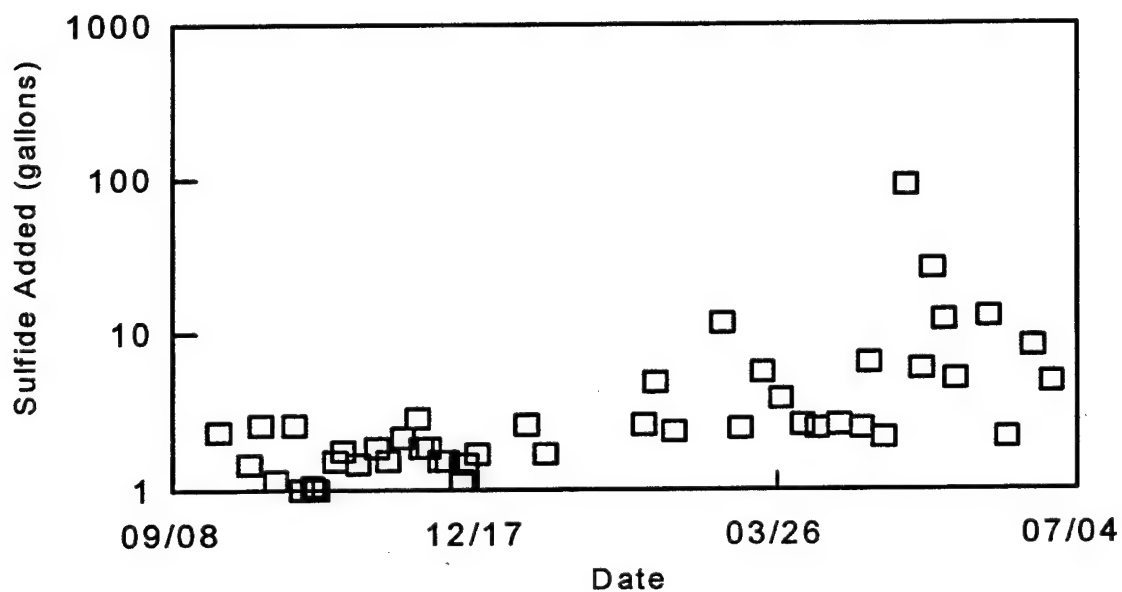
**Figure 19** Volume of Wastewater Treated during the Operation of the SS/FS Process at the NUWC IWTP.



**Figure 20** Influent Hexavalent Chromium Concentration During the Operation of the SS/FS Process at the NUWC IWTP.

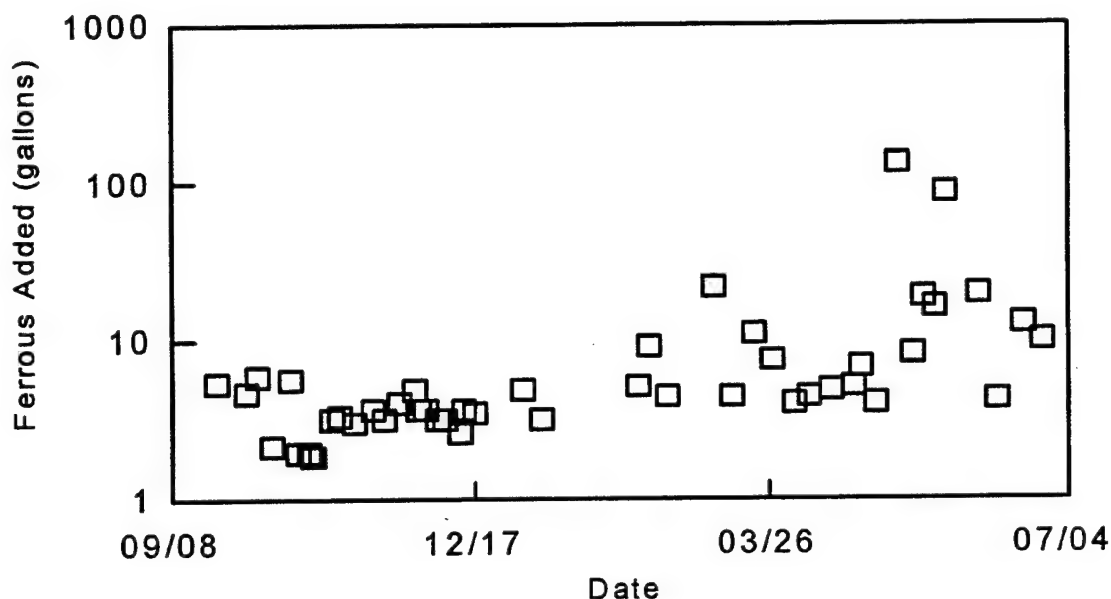


**Figure 21** Influent pH of the Wastewater during Operation of the SS/FS Process at the NUWC IWTP.



**Figure 22** Sulfide Usage during Operation of the SS/FS Process at the NUWC IWTP.





**Figure 23 Ferrous Usage during Operation of the SS/F Process at the NUWC IWTP.**

Table 14 lists the drums of sludge disposed of during operation of the SS/FS Process. The initial drum of sludge was primarily sludge from the Sulfuric Acid/Sulfur Dioxide/Caustic process. Table 15 lists the chemical usage, sludge generated and treatment cost for the Sulfuric Acid/Sulfur Dioxide/Caustic process for the period of a year from October 1993 to September 1994. Table 16 lists the chemical usage, sludge generated and treatment cost for the SS/FS process for a period of nine months from September 22, 1995 to June 26, 1996. The data resulted in average cost savings with the SS/FS process of approximately 34%.

Referring to the influent data summary in Table 13, it is observed that, for the most part, the  $\text{Cr}^{+6}$  concentrations in mg/L are in single digits or less. A comparison of the data indicated a sludge reduction for the SS/FS process of 37% over the  $\text{H}_2\text{SO}_4/\text{SO}_2/\text{Caustic}$  process for low influent concentrations of  $\text{Cr}^{+6}$ . Since March 1966, measured volumes of high  $\text{Cr}^{+6}$  anodize strip solution were added to several batches of influent wastewater, thus raising the  $\text{Cr}^{+6}$  in mg/L to

double digits and on one occasion to 100 mg/L. On May 8, 1996, an excursion in the plating shop resulted in an influent  $\text{Cr}^{+6}$  concentration of 310 mg/L. At these high  $\text{Cr}^{+6}$  levels, the sodium

Table 14. Sludge Generation with the SS/FS Process at the NUWC IWTP		
Date	Drum #	Accumulated Drums of SS/FS Sludge
10/4/94	1	
11/22/95	2	1
11/29/95	3	2
12/22/95	4	3
1/9/96	5	4
2/9/96	6	5
2/16/96	7	6
2/22/96	8	7
2/26/96	9	8
3/4/96	10	9
3/8/96	11	10
3/18/96	12	11
3/21/96	13	12
3/27/96	14	13
4/2/96	15	14
4/9/96	16	15
4/10/96	17	16
4/26/96	18	17
4/29/96	19	18
5/13/96	20	19
5/16/96	21	20
5/17/96	22	21
5/28/96	23	22
5/29/96	24	23
6/10/96	25	24
6/11/96	26	25
6/14/96	27	26
6/24/96	28	27
Drum # 1 was Primarily Hydroxide Sludge		

sulfide and ferrous sulfate solutions were added in 4 stages (following the recommended tables in the O&M Report) before  $\text{Cr}^{+6}$  was completely reduced. Comparison with similar anodize strip solution additions with the  $\text{H}_2\text{SO}_4/\text{SO}_2/\text{Caustic}$  process indicated that the sludge reduction with the SS/FS process decreased to about 17%.

Comparison of the cost of chemicals shows that the SS/FS process results in a reduction of chemical costs from \$9,111/yr to \$3,770/yr over the caustic process, a reduction of 59%. Compared with the old caustic process, the SS/FS process resulted in a 31% reduction in sludge disposal costs from \$84,825 to \$58,215 per year. Overall cost savings were \$31,950, which amounted to a 34% total savings per year.

As the influent hexavalent chromium concentration is increased however, the cost savings decrease. The reason for this is two-fold. As the concentration of hexavalent chromium increases, the total ferrous addition to the process increases. At concentrations below 20 mg/L  $\text{Cr}^{+6}$ , the ratio of ferrous iron is normally 1.5 mg/L per 1 mg/L  $\text{Cr}^{+6}$  while at concentrations greater than 20 mg/L  $\text{Cr}^{+6}$  the required ferrous iron concentration is normally 1 mg/L per 1 mg/L  $\text{Cr}^{+6}$  but the total ferrous iron added has increased and this adds to the quantity of sludge generated by the process. This is consistent with data from the pilot plant operation at the PWC, Pensacola. Review of the process data from the NUWC IWTP, however, shows that even greater ferrous iron additions were required for the process.

The increased requirement for the ferrous iron is believed to be due to the presence of phosphates in the influent wastewater which tended to react with the iron in the ferrous sulfate forming iron phosphate, thereby making less iron available to react in the  $\text{Cr}^{+6}$  reduction. The amount of the ferrous sulfate addition was increased as specified in the corrected Table in the O&M Manual.

The early batch runs experienced a high level of turbidity in the effluent from the clarifier. The reasons for this included the tank/mixing paddle interaction discussed earlier;

additional sulfide solutions from unknown sources; a lower than expected sludge circulation rate ( it was increased); a low polymer flow; and a low level of the sludge blanket. The sludge blanket was built up and the change in the polymer back to Betz® 1160X reduced the turbidity levels which are now within acceptable limits.

As noted earlier, a solution to the problem of oxidation of the iron from ferrous to ferric and sulfide to sulfate was to keep the batch size of the wastewater processed small at about 20,000 - 25,000 gallons daily, so that the entire batch could be treated and the cycle completed the same day. Further, as the polymer Betz® 1160X interacted better with the precipitated flocculant, the flow through the clarifier was increased from a nominal 30 gpm to between 50 - 60 gpm, near the maximum capacity for satisfactory clarification. As a result, larger batch sizes of up to about 39,000 gallons were processed routinely.

**Table 15. The Chemical Usage and Sludge Generation with the Sulfuric Acid/Sulfur Dioxide/Caustic Process at the NUWC IWTP**

Chemical	Usage	Cost \$/100,000 gallons
50 % Caustic (55 gallon drum) \$148.15/drum	1.34 drums/100,000 gallons	\$ 198
75 % Sulfuric Acid (55 gallon drum), \$115/drum	0.42 drums/100,000 gallons	\$ 48
Sulfur Dioxide (1 ton cylinder) \$551.80/cylinder	124.14 lbs/100,000 gallons	\$ 34
Betz 1160X (50 lb bag) \$317.16/bag or \$6.34/lb	1.59 lbs/100,000 gallons	\$ 10
Total Chemical Feed Requirement		\$ 290*
Sludge Generation (\$2.786/lb)**	969.13 lbs/100,000 gallons	\$2,700***
Total Treatment Cost		\$2,990

\* The Treatment costs includes cyanide, specialty chemicals, and acid/chromium treatment.

\*\* Hazardous Waste disposal costs includes disposal, analytical, and tracking costs.

\*\*\* Based on prior data, 30,447 lbs per year of sludge was generated using this process while treating 3,141,660 gallons of wastewater. The average weight of sludge per barrel was 327 lbs which would indicate about 2.97 drums of sludge per 100,000 gallons of wastewater.

\*\*\*\* Chemical usage and costs were those obtained for 1993 through 1994. Actual costs were not available for 1995.

**Table 16. Chemical Usage and Sludge Generation with the SS/FS Process\*  
at the NUWC IWTP**

Chemical	Usage	Cost \$/100,000 gallons
Sulfide Solution (150,000 mg/L S <sup>2-</sup> ) (\$0.36/lb)	74.98 lbs/100,000 gallons	\$ 27
Ferrous Sulfate Heptahydrate (FeSO <sub>4</sub> •7H <sub>2</sub> O) \$0.29/lb if bought as 20 bag lots (50 lb/bag)	36.6 lbs/100,000 gallons	\$ 11
50 % Caustic (\$148.15/55 gal drum)	0.17 dr/100,000 gallons	\$ 25
75 % Sulfuric Acid (\$115/55 gal drum)	0.45 gal/100,000 gallons	\$ 1
Betz 1195 Cationic Polymer (\$2.5/lb) 25 mg/L	20.8/100,000 gallons	\$ 52
Betz 1120 Anionic Polymer (\$5/lb) 1 mg/L	0.83/100,000 gallons	\$ 4
Total Chemical Cost		\$ 120
Sludge generation (assumes 326 lbs/drum) (\$2.786/lb) 0.67 drums/100,000 gallons	665 lbs/100,000 gallons	\$1,853
Total Treatment Cost		\$1,973
Cost Savings	34 %	\$1,017

\* Chemical usage and costs are based on the actual volume of sulfide and ferrous used during treatment from September 22, 1995 through June 26, 1996. Sludge generation was based on the same time period (See Table 13).  
Chemical costs were based on costs for buying bulk quantities of the chemical. Caustic and Sulfuric acid usage are projected as no quantities were actually available.  
Polymer requirements are based on the use of Betz 1195 and 1120. Keyport had switched to Betz 1160X, which works out to be a little cheaper than Betz 1195 and 1120.

The NUWC IWTP met all of their discharge requirements during operation of the SS/FS process at Keyport. Based on tests conducted at the PWC, Pensacola and the IWTP, Keyport, the capability of the SS/FS process to meet current and proposed limits is shown in Table 17. The existing and proposed pretreatment limits (40 CFR Part 433) for Metal Products and Machinery (MP&M), which includes electroplating/metal finishing, can be easily met by the SS/FS process. It is possible that when excess iron is added in the process, there could be an increase in the

<b>Table 17. Capability of SS/FS Process to Meet Effluent Limits</b>				
<b>Pollutant Metal</b>	<b>Existing Pre- treatment Limit mg/L</b>	<b>Proposed Pre- treatment Limit mg/L</b>	<b>NPDES Limit mg/L</b>	<b>SS/FS Process Effluent mg/L</b>
Aluminum(new)	NR	1.40	NR	NA
Cadmium	0.69	0.70	0.028	0.010
Chromium	0.30	0.30	0.050	0.031
Copper	3.38	1.30	0.015	0.010
Iron(new)	NR	2.40	NR	0.380
Lead	0.60	NA	0.050	0.004
Nickel	3.98	1.10	0.100	0.094
Silver	0.43	NA		0.002
Zinc	2.61	0.80	1.000	0.102
<b>NA - Not Available; NR - Not Regulated</b>				

concentration of iron in the effluent. However, iron is not currently listed in the discharge requirements. Table 17 also indicates that the SS/FS process can adequately meet the current National Pollutant Discharge Elimination System (NPDES) requirements.

The IWTP personnel at NUWC Keyport were pleased with the operation of the SS/FS process. The substantially decreased reaction time over the  $H_2SO_4/SO_2$ /Caustic process allowed rapid reduction of hexavalent chromium. This permitted both treatment and clarification during the same day. IWTP personnel were pleased that the process readily handled changes in the influent heavy metals, such as, copper, and simultaneously handled the metals from the cyanide process as well. The operators were also pleased that the two 2-ton bottles of  $SO_2$  were removed from the shop, thereby eliminating safety concerns. NUWC, Keyport intends to continue to use the SS/FS process at the IWTP in the future.

## **6.0 SAFETY CONSIDERATIONS**

Operation and maintenance of the NUWC IWTP requires operators to handle or be exposed to potentially hazardous chemicals. Personnel should be familiar with these chemicals and how to prevent injury to themselves and others. This section explains the chemical used in wastewater treatment and describes any special protective measures that should be used. In addition to the precautions described below, personnel should always consult the Material Safety Data Sheets (MSDS) for these or any other chemicals which they may be using and adhere to the precautions described on the MSDS. Personnel should wear safety glasses and faceshields when operating or observing operations in the industrial wastewater treatment plant. Safety glasses and faceshields will be used per ANSI Standard Z87.1 - 1989. Faceshields will be worn only over primary eye protection, otherwise, safety glasses will be used consisting of cups or goggle type with indirect (side) ventilation to provide protection from splash or irritating mists.

### **6.1 BETZ®1120 ANIONIC POLYMER**

Betz®Polymer 1120 is a high charge density, anionic, high molecular weight polymer. It is a free flowing white powder. This product is not hazardous as defined by OSHA Regulations. Spilled polymer is very slippery. Spills should be scooped and/or wiped up before flushing with water. The wet surface may be slippery. This can be controlled by spreading sand or grit.

### **6.2 BETZ®1195 CATIONIC POLYMER**

Betz®Polymer 1195 is a strongly cationic medium molecular weight, liquid coagulant. The product is approved by the EPA for potable use up to 20 mg/L. This product is not hazardous as defined by OSHA Regulations. Spill of this chemical can result in a slippery surface. The spill should be contained on absorbent material and this material placed in a waste disposal container. The area should be flushed with water. The wet area may be slippery. This can be controlled by spreading sand or grit.

### **6.3 FERROUS SULFATE**

Ferrous Sulfate [Ferrous Sulfate Heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) ] is an odorless, blue green crystal. Inhalation may cause irritation of the respiratory tract. Ferrous sulfate can cause skin irritation or eye irritation. Wash the affected area immediately with water until no evidence of the chemical remains. Employee must wear appropriate protective (impervious) clothing and equipment to prevent repeated or prolonged skin contact with this substance and splash-proof or dust-resistant safety goggles and a face shield to prevent contact with this substance. Sulfuric acid is added to the water prior to the ferrous sulfate addition to maintain the iron in the ferrous state. Therefore, the safety requirements for sulfuric acid should apply to the ferrous solution.

### **6.4 SODIUM HYDROXIDE**

Sodium hydroxide ( $\text{NaOH}$ ) is caustic in solid form and even more so in water solution. Contact with the skin can quickly cause severe burns. As with other chemicals, accidentally exposed skin should be immediately flooded with running water, and prompt medical treatment should be obtained. During maintenance or repair of the  $\text{NaOH}$  pumps, piping, or tanks, personnel should wear base-protective clothing (butyl rubber or polyethylene suit, gloves, and boots) and a full-face shield.

### **6.5 SULFURIC ACID**

Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is a very corrosive liquid that, in concentrated solution, reacts violently with water and will dehydrate and char the skin. Contact with the liquid or its vapor should be avoided. In case of accidental exposure, flood the affected area immediately with running water and follow established procedures for obtaining medical care as quickly as possible. During maintenance or repair of the sulfuric acid pumps, piping, or tanks, personnel should wear acid-protective clothing (butyl rubber or polyethylene suit, gloves, and boots) and a full-face shield.



## 6.6 SODIUM SULFIDE AND HYDROGEN SULFIDE

Sodium Sulfide is a corrosive solid and contact with the skin, especially if wet, should be avoided. If contact with the skin should occur, immediately flood the affected area with water. Sodium Sulfide reacts with acids to form hydrogen sulfide ( $H_2S$ ), which is a colorless, very toxic gas that can be easily detected in concentrations of about 10ppm because of the smell of rotten eggs.  $H_2S$  gas can react with the water on mucous membranes, such as, the lining of the nose, eyes and lungs, to form sulfuric acid that can cause serious burns. The gas is heavier than air and settles in low places such as pits and basements.

Hydrogen Sulfide is a flammable gas with a lower heating value of 595 BTU/ft<sup>3</sup>. Its lower and upper flammability limits, i.e. the minimum and maximum percentages of  $H_2S$  in a  $H_2S$ -air mixture which will burn, are 4.3 and 45.5%  $H_2S$  by volume. Within these limits,  $H_2S$ -air mixture will spontaneously ignite at a temperature of 558°F. Fortunately, the human nose is very sensitive and the odor of rotten eggs can be detected at much below the lower flammability limit.

When operating the IWTP on the SS/FS process, care must be taken to ensure that the influent wastewater, if acidic, is first neutralized by the addition of caustic before sodium sulfide is metered to the wastewater. For this reason, the influent pH is monitored and controlled by a dual set point relay for between pH of 7.2 and 7.8. This control system uses a relay card to sound the annunciator system (horn and light) when the pH is outside the SS/FS operating range.

It was recommended that the IWTP install an automatic  $H_2S$  detection/monitoring system in the event that a catastrophic failure in the control system occurred and  $H_2S$  was released. The IWTP is equipped with a  $SO_2$  detector and alarm system made by Mine Safety Appliances. It was recommended that a  $H_2S$  detector manufactured by Mine Safety be installed and wired to the existing alarm system for a total cost of \$1,500.

## **7.0 OPERATOR TRAINING**

Implementation of the SS/FS process requires operator training. Training included review of the operational procedure prior to start up and on-site training of the operational personnel during the process start-up. During the on-site training, ERAD and PAR personnel instructed the operators through each step of the operation as it was performed. On-site training occurred over a period of a week. At the end of the week, operation was turned over to the NUWC Industrial Wastewater Treatment Plant personnel. Over the next several weeks, as changes occurred during the operation or occurred in the wastewater, the operators consulted with PAR/ERAD staff via telephone, on an as needed basis.

The IWTP staff were provided an Operation and Maintenance (O&M) manual, which served as a reference manual. The O&M manual contained a description of all equipment modifications to the existing plant, instrumentation and calibration methods, procedures for preparation of the chemical feeds, tables for the chemical feed requirements as a function of hexavalent chromium concentration, safety precautions, and a troubleshooting guide. Instrument and equipment manufacturer's specifications and literature were also provided in a separate file.

Operator Training is not an extensive program. In general, if the operators are familiar with normal industrial wastewater treatment procedures, they easily adapt to the use of the SS/FS treatment process. Normally, they find the process much easier to operate than conventional wastewater treatment processes.

## 8.0 CONCLUSIONS AND RECOMMENDATIONS

The application and economics of the SS/FS process to the treatment of the heavy metal bearing industrial wastewater generated at the NUWC was evaluated. Cost comparison of the SS/FS process with the existing Sulfuric Acid/Sulfur Dioxide/Caustic process shows a 59 % reduction in chemical treatment costs (from \$9,111/yr to \$3,770/yr) and a 31 % reduction in the sludge disposal cost ( from \$84,825 to \$58,215) could be realized with the implementation of the SS/FS process. This is an overall cost savings of \$31,950/yr or 34 % of the chemical treatment cost and sludge disposal cost.

The discharge from the SS/FS process readily met the discharge requirements for the NUWC IWTP. However, a comparison of the metal concentrations in the effluent of the SS/FS process to the previous Sulfuric Acid/Sulfur Dioxide/Caustic process could not be made, as the analytical analysis was not available for the previous process.

It is recommended that the industrial wastewater treatment process be reviewed at other Naval IWTPs where the implementation of the SS/FS process could result in similar or larger cost savings.

### 8.1 PROCESS ADVANTAGES

The SS/FS process offers several advantages over the conventional sulfur dioxide or sodium sulfite reduction of hexavalent chromium at pH 2 to 3 and heavy metal precipitation with caustic or lime. These include the following:

- Acidic reduction of hexavalent chromium with sulfur dioxide or sodium sulfite becomes less efficient as the hexavalent chromium concentration decreases below 1 to 0.5 mg/L  $\text{Cr}^{+6}$ . The reduction is slower and requires more of the sulfur dioxide or sodium sulfite. In many cases where the discharge limit for the total chromium is 0.1 mg/L or less, the

hexavalent chromium can not be reduced to discharge concentration. Hexavalent chromium reduction does not become limited at the lower hexavalent chromium concentration with the SS/FS process. Even at low hexavalent chromium concentration (0.5 mg/L  $\text{Cr}^{+6}$  or less) the chromium reduction is instantaneous with the SS/FS process..

- Acidic reduction of hexavalent chromium with sulfur dioxide or sodium sulfite requires tank retention times of 45 minutes to complete the reduction. The long retention time required for the reduction increases the size of the wastewater treatment plant significantly. In plants using the acidic reduction of the hexavalent chromium, there is generally a mixer tank for sulfuric acid and sulfur dioxide or sulfite addition having a retention time of 45 minutes, a second tank for caustic addition (pH adjustment) having a retention time of 45 minutes, and a third tank having a retention time of 10 to 20 minutes. Depending on the flow through the wastewater treatment plant, these tanks may require considerable space. Because the reactions which occur in the SS/FS process are instantaneous, the large tanks are not required. Actually, static mixers can be used to replace the large tanks, so that the whole chromium reduction, heavy metal precipitation process occurs in the pipe.
- The SS/FS process is completed at neutral pH (pH 7.2 to 8.4). This reduces significantly the requirement for sulfuric acid and caustic or lime. The only caustic required is to ensure the initial reaction pH is greater than 7.2 prior to sulfide addition. Acid may be required to control the pH after sulfide and ferrous addition. This is in contrast to the conventional reaction where the pH is lowered with sulfuric acid to 2 to 3 for chromium reduction, raised to 8.5 to 12 with caustic or lime for metal precipitation (this pH is dependent on metals being precipitated) and again lowered with sulfuric acid to pH 6 to 9 for discharge.
- The SS/FS process is able to meet much lower discharge standards than the hydroxide precipitation processes. The lower concentrations of heavy metals in the final effluent is

due to the orders of magnitude lower solubility of the metal sulfides in contrast to the metal hydroxides. The pH of minimum solubilities of the hydroxides varies from 7.5 to 12 depending on the metals present and surfactants which may be present in the industrial wastewater. This is not true with the metal sulfides. Additionally, the impact seen from the presence of surfactants in the wastewater is significantly less with the SS/FS process.

- Microfiltration can be incorporated into the SS/FS process, thereby further minimizing the IWTP size. The Microfiltration is currently being demonstrated in an Army Phase II SBIR (Reference 21).

There are other additional benefits that the Sodium Sulfide /Ferrous Sulfate process offers to the IWTP and these are:

- The SS/FS process operation was able to reduce all  $\text{Cr}^{+6}$  that could slip through with the cyanide plant effluent, unlike the conventional process operation, thus avoiding potential violations of the discharge limits. The reason for this is that the conventional process does not treat the wastewater for  $\text{Cr}^{+6}$  reduction if no  $\text{Cr}^{+6}$  is shown to be present. The SS/FS process always treats for  $\text{Cr}^{+6}$ , even if none is shown to be present .
- In the hydroxide process, detergents present in the influent would interact with the  $\text{SO}_2$  requiring more sulfur dioxide usage to reduce the hexavalent chrome. This proved expensive. With the SS/FS process, the presence of detergents required some additional ferrous sulfate usage but ferrous sulfate is cheap compared with sulfur dioxide.
- The old process required that two 2 ton tanks of  $\text{SO}_2$  be kept at the plant. This presented a safety problem. By shifting to the SS/FS process, the tanks were disposed off, thus eliminating the safety problem.

- The fact that the SS/FS process operated at neutral pH results in longer tank life compared with the sulfuric acid/sulfur dioxide/caustic process which corroded the tanks due to acidic conditions.
- The SS/FS process also required less acid and caustic to be purchased and stored on site.
- Because the SS/FS process reduced hexavalent chrome instantaneously, the overall processing time was reduced. This allowed the operators to treat and clarify each batch on the same working day.

## **8.2 REQUIREMENTS FOR IMPLEMENTATION**

The SS/FS process can easily and economically be implemented into existing wastewater treatment plants. The modifications required for the NUWC Keyport IWTP would generally be the same as required for other existing facilities. The exception would be the sludge recirculation line and the clarifier skirt modifications. These modifications would be dependent on the conditions of the existing clarifiers at these facilities.

The addition of the streaming current detector and the turbidity meter is not required by the process. However, these two instruments are very beneficial in the control of the effluent quality. These additions would be beneficial to existing sulfur dioxide/caustic processes. Moving and modifying the pH probe and sample collection was required because the probe was not located conveniently even for the existing Sulfuric Acid/Sulfur Dioxide/Caustic Process.

The primary plant addition required by the SS/FS process is the chemical feed systems for the sodium sulfide solution and the ferrous sulfate solutions. Normally, even if there is existing piping and pumps for these chemical feed systems, the pumps need to be sized down due to the small chemical feed requirements. Additionally, the acid feed may require a smaller pump as the volume of acid is reduced significantly by the implementation of the SS/FS process. The polymer

feed is likewise reduced and a smaller polymer pump may be required. All the modifications done at the NUWC IWTP are shown in Figure 18 (Section 4.0) and explanations are given for each item of new hardware or new parts that required modification.

The cost savings at NUWC Keyport were about \$32,000 per year. The cost to install the demonstration was about \$230,000. The cost of future implementations at other Naval IWTPs may be more or even significantly less depending upon individual site characteristics, processes employed, amounts of effluent treated, sludge generated and other site specific factors.

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## APPENDIX A

### SAMPLE OF JAR TEST PARAMETERS AND TEST RESULTS

JAR TEST SET # 1					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	14	14	7.2	10	0.5
2	14	16	7.2	10	0.5
3	14	18	7.2	10	0.5
4	14	20	7.2	10	0.5
5	14	24	7.3	10	0.5
Excellent floc formation.					
Definitely Cr+6 remaining					
Test	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)			
1	20	10.00			
2	19	9.50			
3	17	9.50			
4	17	9.50			
5	17	8.50			

JAR TEST SET # 2					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	27	18	7.2	10	0.5
2	27	22	7.3	10	0.5
3	27	27	7.3	10	0.5
4	27	30	7.3	10	0.5
5	27	34	7.3	10	0.5
6	27	36	7.3	10	0.5
Test	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)			
1	10	5.25			
2	9	4.75			
3	8	3.46			
4	6	2.66			
5	0	0.58			
6	0	0.46			

JAR TEST SET # 3					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	36	18	7.2	10	0.5
2	36	22	7.2	10	0.5
3	36	27	7.2	10	0.5
4	36	30	7.2	10	0.5
5	36	34	7.2	10	0.5
6	36	36	7.2	10	0.5
Test	Filtered Turbidity (FTU)	Cr+6 (mg/L)	Total Cr (mg/L)	Total Fe (mg/L)	
1	2	0.33	1.92	0.00	
2	1	0.01	0.05	0.03	
3	0	0.01	0.03	0.08	
4	0	0.01	0.03	0.11	
5	0	0.01	0.03	0.20	
6	0	0.01	0.02	0.32	
At 0.01 hexavalent chromium, no color was visible					

JAR TEST SET # 4					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	30	18	7.3	10	0.5
2	30	22	7.3	10	0.5
3	30	27	7.3	10	0.5
4	30	30	7.3	10	0.5
5	30	34	7.3	10	0.5
6	30	36	7.3	10	0.5
4 looks like the sulfide was doubled.					
Test	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)	Total Fe (mg/L)		
1	11	4.80	0.05		
2	10	4.30	0.06		
3	0	0.56	0.03		
4	0	--	--		
5	0	0.01	0.05		
6	0	0.01	0.04		
At 0.01 hexavalent chromium, no color was visible					

Test 4-4, 3-1 and 3-2 Rerun.					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	30	30	7.3	10	0.5
2	36	18	7.3	10	0.5
3	36	22	7.3	10	0.5
Test	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)	Total Fe (mg/L)		
1	0	0.01	0.03		
2	0	0.01	0.02		
3	0	0.01	0.03		
No color was visible at 0.01 mg/L Cr+6					

JAR TEST SET # 5					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	36	18	7.2	0	0.5
2	36	18	7.2	5	0.5
3	36	18	7.2	10	0.5
4	36	18	7.2	15	0.5
5	36	18	7.2	20	0.5
6	36	18	7.2	25	0.5
1. Glomps together-- large floc formation					
2. Large floc formation, doesn't glomp as much as # 1.					
3-6. All have large floc. Slower to settle than 1 and 2.					
Test	Unfiltered Turbidity (FTU)	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)		
1	4		over range		
2	7		0.24		
3	8		0.29		
4	7		0.36		
5	5		0.09		
6	6		0.45		
All still have Cr+6 remaining.					



JAR TEST SET # 6					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	36	22	7.2	10	0.5
2	36	27	7.2	10	0.5
Test	Unfiltered Turbidity (FTU)	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)	Total Fe (mg/L)	
1			0.00		
2			0.01		
Selected 2 as the optimum sulfide and ferrous feed. Allows for some variation in the wastewater.					

JAR TEST SET # 7					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	36	27	7.3	0	0.5
2	36	27	7.3	5	0.5
3	36	27	7.3	10	0.5
4	36	27	7.3	15	0.5
5	36	27	7.3	20	0.5
6	36	27	7.3	25	0.5
First two -- clearing even on high stirring.					
All have good floc formation; 1 and 2 are definitely clearer.					
Test	Unfiltered Turbidity (FTU)	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)	Total Cr (mg/L)	Total Fe (mg/L)
1	10	6	BDL	0.04	0.20
2	3	2	BDL	0.01	0.07
3	9	2	BDL	0.03	0.08
4	10	3	BDL	0.04	0.08
5	10	3	BDL	0.05	0.10
6	11	4	BDL	0.06	0.10
At 0.01 total chromium, there is a tinge of pink.					

JAR TEST SET # 8					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	36	27	7.5	0	0.25
2	36	27	7.5	0	0.50
3	36	27	7.5	0	1.00
4	36	27	7.5	0	2.00
5	36	27	7.5	0	3.00
6	36	27	7.5	0	4.00
All except 1 shows clearing upon polymer addition.					
1 definitely does not have enough polymer					
4, 5, and 6 settles immediately.					
Test	Unfiltered Turbidity (FTU)	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)	Total Cr (mg/L)	Total Fe (mg/L)
1	10	10	BDL	0.03	0.11
2	10	4	BDL	0.03	0.08
3	6	0	BDL	0.03	0.00
4	3	2	BDL	0.04	0.07
5	7	4	BDL	0.05	0.14
6	9	9	BDL	0.06	0.16

JAR TEST SET # 9					
Test	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1160x (mg/L)	Betz® 1120 (mg/L)
1	36	27	7.2	5	0.00
2	36	27	7.2	10	0.00
3	36	27	7.2	15	0.00
4	36	27	7.2	20	0.00
5	36	27	7.2	25	0.00
6	36	27	7.2	30	0.00
1 and 6 are dark in color					
The remaining jars looks great.					
6 looks clear after slow stir, floc balls together.					
1 has large floc, Rest has real large floc.					
Test	Unfiltered Turbidity (FTU)	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)	Total Cr (mg/L)	Total Fe (mg/L)
1	9	0	BDL	0.04	1.50
2	8	0	BDL	0.03	1.75
3	5	0	BDL	0.03	2.12
4	3	1	BDL	0.02	1.82
5	7	0	BDL	0.02	1.10
6	10	0	BDL	0.03	1.55

JAR TEST SET # 10

1 liter samples were used.

Test	S-2 (mg/L)	Fe+2 (mg/L)	pH (unit)	Betz 1195 (mg/L)	Betz 1120 (mg/L)
1	36	27	7.2	0	3.00
2	36	27	7.2	0	3.00
3	36	27	7.2	0	3.00
4	36	27	7.2	5	0.50
5	36	27	7.2	5	0.50
6	36	27	7.2	5	0.50

1 through 3, water is murky, unfiltered turbidity is 22.

In original test, there must have been some residual cationic polymer remaining on the stirrer paddles.

4 through 6 unfiltered turbidity was 3 FTU

Sludge weight was determined from 4 through 6.

Test	Dry Tare Weight (grams)	Wet Tare Weight (grams)	Wet Weight Filter and Sludge (grams)	Dry Weight Filter and Sludge (10 min) (grams)	Dry Weight Filter and Sludge Overnight (grams)
4	1.0799	1.4550	3.6642	2.6750	1.4286
5	1.1023	1.6397	3.3238	2.7720	1.4515
6	1.0924	1.7012	3.8314	2.4512	1.4677
Test	Sludge Wet Weight (g/L)		Sludge Dry Weight (10 min) (g/L)		Sludge Dry Weight overnight (g/L)
4	2.2092		1.5951		0.3487
5	1.6841		1.6697		0.3492
6	2.1302		1.3588		0.3753

JAR TEST SET # 11						
Test	Influent Cr <sup>+6</sup> (mg/L)	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	17	34	25.5	7.4	5	0.50
2	25	50	37.5	7.4	5	0.50
3	50	100	75.0	7.4	10	0.50
4	100	200	150.0	7.4	10	0.50
5	250	500	375.0	7.3	10	0.50
6	500	1000	750.0	7.4	10	0.50
Test	Filtered Turbidity (FTU)	Cr+6 (mg/L)	Total Cr (mg/L)	Total Fe (mg/L)		
1	0	BDL	0.04	0.08		
2	2	BDL	0.03	0.08		
3	0	BDL	0.03	0.19		
4	0	BDL	0.04	0.24		
5	0	BDL	0.02	1.61		
6	0	BDL	0.01	>3.0		

JAR TEST SET # 12						
Test	Influent Cr <sup>+6</sup> (mg/L)	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	25	25	25	7.3	10	0.50
2	50	50	50	7.4	10	0.50
3	100	100	100	7.3	10	0.50
4	250	250	250	7.3	10	0.50
5	500	500	500	7.4	10	0.50
Test	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)	Total Cr (mg/L)	Total Fe (mg/L)		
1	3	BDL	0.03	0.08		
2	0	BDL	0.03	0.08		
3	0	BDL	0.05	0.08		
4	0	BDL	0.04	0.69		
5	1	BDL	0.06	2.38		
There was no color visible on any of the total chromium						

JAR TEST SET # 13

Test	Duraclean (volume %)	S <sup>-2</sup> (mg/L)	Fe <sup>+2</sup> (mg/L)	pH (unit)	Betz® 1195 (mg/L)	Betz® 1120 (mg/L)
1	0.0	34	25.5	7.5	5	0.50
2	0.1	34	25.5	7.4	5	0.50
3	0.2	34	25.5	7.5	5	0.50
4	0.5	34	25.5	7.5	5	0.50
5	1.0	34	25.5	7.4	5	0.50
6	2.0	34	25.5	7.3	5	0.50

Precipitate fine throughout.

6 is getting a little sudsy.

Test	Unfiltered Turbidity (FTU)	Filtered Turbidity (FTU)	Cr <sup>+6</sup> (mg/L)	Total Cr (mg/L)	Total Fe (mg/L)	
1	7	0	BDL	0.03	0.05	
2	7	2	BDL	0.03	0.15	
3	9	2	BDL	0.05	0.16	
4	11	3	BDL	0.12	0.47	
5	11	5	BDL	0.30	0.97	
6	12	6	BDL	0.61	2.56	



APPENDIX B

LAUCKS TESTING LABORATORIES, INC.

SAMPLE OF ANALYTICAL REPORT

# Laucks

## Testing Laboratories, Inc.

940 South Harney St., Seattle, WA 98108 (206) 767-5060 FAX (206) 767-5063

Chemistry, Microbiology, and Technical Services

CLIENT: Pacific Western Services, Inc  
3594 NW Byron St., Suite 202  
P.O. Box 3043  
Silverdale, WA 98383-3043  
ATTN : Fred Inboden

### Certificate of Analysis

Work Order# : 94-05-439  
DATE RECEIVED : 05/10/94  
DATE OF REPORT: 05/23/94

Work ID : Inorganic Analysis  
Taken By : Client  
Transported by: Hand Delivered  
Type : Water

#### SAMPLE IDENTIFICATION:

	<u>Sample</u> <u>Description</u>	<u>Collection</u> <u>Date</u>
01	4130-01-02-03-04 Bldg #825	05/10/94 06:30

#### FLAGGING:

The flag "U" indicates the analyte of interest was not detected, to the limit of detection indicated.

#### ATTACHMENTS:

Following presentation of sample results, the following appendices are attached to this report:

- Appendix A: Method Blank Report
- Appendix B: MS/MSD & Duplicate Reports
- Appendix C: Blank Spike Recovery Report
- Appendix D: Chain-of-Custody



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Chemistry, Microbiology, and Technical Services

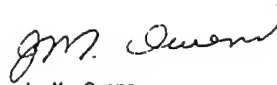
CLIENT : Pacific Western Services, Inc

### Certificate of Analysis

Work Order# : 94-05-439

Unless otherwise instructed all samples will be discarded on 07/08/94

Respectfully submitted,  
Laucks Testing Laboratories, Inc.

  
J. M. Owens



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## Testing Laboratories, Inc.

940 South Harney St., Seattle, WA 98108 (206) 767-5060 FAX (206) 767-5063

Chemistry, Microbiology, and Technical Services

CLIENT : Pacific Western Services, Inc

### Certificate of Analysis

Work Order # 94-05-439

#### TESTS PERFORMED AND RESULTS:

Analyte	Units	<u>01</u>
Aluminum (Method 6010)	mg/L	0.11
Antimony (Method 6010)	mg/L	0.006 U
Arsenic (Method 6010)	mg/L	0.020 U
Barium (Method 6010)	mg/L	0.003
Beryllium (Method 6010)	mg/L	0.001 U
Cadmium (Method 6010)	mg/L	0.018
Calcium (Method 6010)	mg/L	18.
Chromium (Method 6010)	mg/L	0.051
Chromium, Hexavalent	mg/L	0.048
Cobalt (Method 6010)	mg/L	0.002 U
Copper (Method 6010)	mg/L	0.012
Cyanide, Total (335.3)	mg/L	0.024
Iron (Method 6010)	mg/L	0.051
Lead (Method 6010)	mg/L	0.005 U
Magnesium (Method 6010)	mg/L	18.
Manganese (Method 6010)	mg/L	0.014
Mercury (Method 6010)	mg/L	0.010 U



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Chemistry, Microbiology, and Technical Services

CLIENT : Pacific Western Services, Inc

### Certificate of Analysis

Work Order # 94-05-439

Continued From Above

#### TESTS PERFORMED AND RESULTS:

Analyte	Units	<u>01</u>
Nickel (Method 6010)	mg/L	0.031
Potassium (Method 6010)	mg/L	8.2
Selenium (Method 6010)	mg/L	0.020 U
Silver (Method 6010)	mg/L	0.001 U
Sodium (Method 6010)	mg/L	420.
Thallium (Method 6010)	mg/L	0.020 U
Total Suspended Solids	mg/L	5.
Vanadium (Method 6010)	mg/L	0.005 U
Zinc (Method 6010)	mg/L	0.010



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Chemistry, Microbiology, and Technical Services

### Quality Control Report Method Blanks for Work Order 9405439

Blank Name	Samples Verified	Test Description	Result	Units	Control
					Limit
B051194_CR6_W01	1	Hexavalent Chromium	0.0050 U	mg/L	0.010
B051194_TSS_W01	1	Total Suspended Solids	2.0 U	mg/L	4.0
B051294_ICP_W02	1	Aluminum by ICP	0.010 U	mg/L	0.050
		Nickel by ICP	0.0020 U		0.0040
		Zinc by ICP	0.0010 U		0.0050
		Silver by ICP	0.0010 U		0.0020
		Arsenic by ICP	0.020 U		0.040
		Barium by ICP	0.0020 U		0.0040
		Beryllium by ICP	0.0010 U		0.0020
		Calcium by ICP	0.10 U		0.20
		Cadmium by ICP	0.0010 U		0.0020
		Cobalt by ICP	0.0050 U		0.010
		Chromium by ICP	0.0010 U		0.0020
		Copper by ICP	0.0010 U		0.0020
		Iron by ICP	0.010 U		0.050
		Mercury by ICP	0.010 U		0.050
		Potassium by ICP	0.10 U		0.20
		Magnesium by ICP	0.10 U		0.20
		Manganese by ICP	0.0010 U		0.0020
		Sodium by ICP	0.10 U		0.20
		Lead by ICP	0.0050 U		0.010
		Antimony by ICP	0.0060 U		0.012
		Selenium by ICP	0.020 U		0.040
		Thallium by ICP	0.020 U		0.040
		Vanadium by ICP	0.0050 U		0.010
B051994_CN_W02	1	Total Cyanide	0.0050 U	mg/L	0.010

A method blank can validate more than one analyte on more than one work order. The method blanks in this report may validate analytes not determined on this work order, but nonetheless determined in the associated blank.

Because they validate more than one work order, method blank results are not always reported in the same concentration units or to the same detection limits that are used for sample results.

\* = blank exceeds control limit



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Chemistry, Microbiology, and Technical Services

### Quality Control Report MS/MSD Report for Work Order 9405439

MS/MSD Name	Sample Fractions Verified	MS/MSD Sample	Analyte	Percent Recovery			Cont. Limits		
				MS	MSD	RPD	LCL	UCL	RPD
K051194_CR6W01	1	9405485-01	Hexavalent Chromium	84	92	9	50	148	30
K051294_ICPW02	1	9405310-01	Silver	101	101	0	50	133	16
			Aluminum	99	99	1	50	147	27
			Arsenic	101	100	2	82	122	11
			Barium	99	98	1	76	112	16
			Beryllium	110	108	2	79	132	10
			Cadmium	91	95	4	70	127	14
			Cobalt	94	95	1	81	115	16
			Chromium	100	103	3	75	117	21
			Copper	99	99	0	77	116	10
			Iron	91	92	1	50	150	30
			Mercury	93	96	3	64	115	13
			Potassium	102	101	1	75	123	12
			Magnesium	109	105	3	50	150	22
			Manganese	112	108	4	59	131	30
			Sodium	104	100	4	50	150	29
			Nickel	95	95	0	77	115	10
			Lead	97	97	0	69	127	18
			Antimony	94	94	0	71	131	29
			Selenium	98	98	1	74	137	24
			Thallium	93	90	4	72	113	10
			Vanadium	97	97	0	84	115	17
			Zinc	96	98	2	68	131	20
K051994_CNW02	1	9405711-01	Cyanide	106	105	1	64	135	11

\* = Value Exceeds Control Limit

RPD = Relative Percent Difference

LCL = Lower Control Limit

UCL = Upper Control Limit

-1 for recovery value indicates that recovery could not be calculated

An MS/MSD pair can validate the results for more than one work order. For this reason, results for analytes not requested on this work order may appear in this MS/MSD report.



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Chemistry, Microbiology, and Technical Services

Quality Control Report  
Duplicate Report for Work Order 9405439

Duplicate Name	Sample Fractions Verified	Sample	Analyte	RPD	Limit
D051194_TSSW01	1	9405432-01	Total Suspended Solids	15	30

\* = Value Exceeds Control Limit  
RPD = Relative Percent Difference  
L = RPD control limit for this analyte is 5x the detection limit. The value appearing in the RPD column is the absolute difference of the duplicates.  
-1 for recovery value indicates that recovery could not be calculated

A duplicate pair can validate the results for more than one work order. For this reason, results for analytes not requested on this work order may appear in this duplicate report.



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Chemistry, Microbiology, and Technical Services

Quality Control Report  
MS/MSD Report for Work Order 9405439

MS/MSD Name	Sample Fractions Verified	MS/MSD Sample	Analyte	Percent Recovery		Cont. Limits				
				MS	MSD	RPD	LCL	UCL	RPD	
K051194_CR6W01	1	9405485-01	Hexavalent Chromium	84	92	9	50	148	30	
K051294_ICPW02	1	9405310-01	Silver	101	101	0	50	133	16	
			Aluminum	99	99	1	50	147	27	
			Arsenic	101	100	2	82	122	11	
			Barium	99	98	1	76	112	16	
			Beryllium	110	108	2	79	132	10	
			Cadmium	91	95	4	70	127	14	
			Cobalt	94	95	1	81	115	16	
			Chromium	100	103	3	75	117	21	
			Copper	99	99	0	77	116	10	
			Iron	91	92	1	50	150	30	
			Mercury	93	96	3	64	115	13	
			Potassium	102	101	1	75	123	12	
			Magnesium	109	105	3	50	150	22	
			Manganese	112	108	4	59	131	30	
			Sodium	104	100	4	50	150	29	
			Nickel	95	95	0	77	115	10	
			Lead	97	97	0	69	127	18	
			Antimony	94	94	0	71	131	29	
			Selenium	98	98	1	74	137	24	
			Thallium	93	90	4	72	113	10	
			Vanadium	97	97	0	84	115	17	
			Zinc	96	98	2	68	131	20	
K051994_CNW02	1	9405711-01	Cyanide	106	105	1	64	135	11	

\* = Value Exceeds Control Limit  
RPD = Relative Percent Difference  
LCL = Lower Control Limit  
UCL = Upper Control Limit  
-1 for recovery value indicates that recovery could not be calculated

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## CHAIN OF CUSTODY RECORD

WORK ORDER ID#

9405439

DATE 5-10-94 PAGE 1 OF 1

THIS INFORMATION WILL BE USED FOR REPORTING/BILLING\* (SEE BELOW)

NAME:

N.V.W.C., Keyport

ADDRESS:

56 D. HANSEN Bldg #95  
ENVIRONMENTAL Div.

ATTENTION:

D. HANSEN

PROJECT NAME:

PROJECT CONTACT:

TELEPHONE/FAX: (206) 396-2119

JOB/PO. NO.:

SAMPLER (SIGNATURE)

(PRINTED NAME)

John D. Hill John D. Hillis

LAB SAM

SAMPLE ID / LOCATION

DATE

TIME

01-4130 Bldg #825 5/10/94 0630  
02-4130 I I I  
03-4130 I I I  
04-4130 I I I

## TESTS TO PERFORM

TOTAL Susp Solids  
TOTAL Cyanide  
TOTAL Metals  
CT+6

NO. OF CONTAINERS

OBSERVATIONS,  
COMMENTS, SPECIAL  
INSTRUCTIONS

Treated Industrial  
Waste Effluent

I

## INSTRUCTIONS

1. USE ONE LINE PER SAMPLE.
2. BE SPECIFIC IN TEST REQUESTS.
3. CHECK OFF TESTS TO BE PERFORMED FOR EACH SAMPLE.

## BILLING INFORMATION, IF DIFFERENT THAN ABOVE

NAME

ATTN:

ADDRESS

CITY, STATE, ZIP

## TURNAROUND REQUEST

- ☐ 24-48 HRS (100% SUR)  
☐ 5-DAYS (50% SUR)  
☐ STD. 10-14 DAYS  
☐ OTHER

## TOTAL NO. OF CONTAINERS

CHAIN OF CUSTODY SEALS:  
☐ YES ☐ NO ☐ NA

SHIPPED VIA:

☐ UPS ☐ FED-EX ☐ BUS

☐ HAND ☐

TEMPERATURE

☐ AMBIENT ☐ REPRESENTATIVE

RECEIVED BY (SIGN AND PRINT)

DATE  
TIME

5/10/94

Barbara Awar

LAUCKS TESTING LABS

## APPENDIX C

### SS/FS PROCESS TREATMENT DATA LOGS AT THE NUWC IWTP

Treatment Log					
Date	9/22/95	9/28/95	10/3/95	10/6/95	
Time	08:00	07:45	07:45	07:30	
Batch #	5265	5271	5276	5279	
Operator	PGL & RR	PGL & RR	RR & PGL	RR & PGL	
Wastewater Volume (gal)	23,200	20,000	21,600	17,600	
Initial pH	6.8	1.9	6.0	6.3	
Cr <sup>+6</sup> Concentration (mg/L)	1.0		3.0	7.0	
Lab Sample #				5279	
Adjusted pH	7.6		7.7	7.6	
Sodium Sulfide Volume Added (gal)	0.4+1.0+0.5+0.5 = 2.4		1.5	1.7+1.0 = 2.7	
pH after Sulfide Addition	7.6				
Ferrous volume Added (gal)	0.7+1.0+0.5+0.5+2.7		2.7+2.0 = 4.7	3.1+1.5+1.5 = 6.1	
pH After Sulfate Addition	7.6		7.3	8.0	
Final Adjusted pH	7.6				
Final Cr <sup>+6</sup> Concentration (mg/L)	0.00		+Cr <sup>+6</sup>	yes Cr <sup>+6</sup>	
Comments			PO <sub>4</sub> <sup>-3</sup> = 22 mg/L		

Treatment Log					
Date	10/11/95	10/18/95	10/20/95	10/24/95	
Time	07:15	07:45	07:00	07:00	
Batch #	5284	5291	5293	5297	
Operator	RHR/PGL	PGL & RR	RHR/PGL	PGL & RR	
Wastewater Volume (gal)	17,000	17,600	15,040	16,000	
Initial pH	6.0	7.0	2.6	6.0	
Cr <sup>+6</sup> Concentration (mg/L)	0	6.5	0	0.26	
Lab Sample #	5284	825-5291	825-5293	825-5297	
Adjusted pH	7.4	7.4	7.7	7.6	
Sodium Sulfide Volume Added (gal)	1.2	1.7+1.0 = 2.7	1.0	1.1	
pH after Sulfide Addition	8	8.2	8.1		
Ferrous volume Added (gal)	2.2	3.1+1.5+1.0 = 5.6	2.0	2.0	
pH After Sulfate Addition	7.4	7.9	7.4		
Final Adjusted pH	7.4		7.4	7.7	
Final Cr <sup>+6</sup> Concentration (mg/L)	0		0	0	
Comments	PO <sub>4</sub> <sup>-3</sup> = 16.8	PO <sub>4</sub> <sup>-3</sup> = 21.6	PO <sub>4</sub> <sup>-3</sup> = 39.2	PO <sub>4</sub> <sup>-3</sup> = 15.7	

# Treatment Log

Date	10/25/95			
Time	07:10			
Batch #	5298			
Operator	PG&L			
Wastewater Volume (gal)	51,200			
Initial pH	6.1			
Cr <sup>+6</sup> Concentration (mg/L)	0			
Lab Sample #	825-5298-1			
Adjusted pH	7.6			
Sodium Sulfide Volume Added (gal)	1.0			
pH after Sulfide Addition	8.1			
Ferrous volume Added (gal)	1.9			
pH After Sulfate Addition	7.7			
Final Adjusted pH	0			
Final Cr <sup>+6</sup> Concentration (mg/L)	PO <sub>4</sub> <sup>-3</sup> = 21.8			
Comments				

Treatment Log					
Date	10/31/95	11/3/95	11/8/95	11/14/95	
Time	7:45	7:35	6:50	6:50	
Batch #	825-5304	825-5307-1	825-5312	825-5318	
Operator	PGL & RR	PGL & RR	PGL & RR	PGL & RR	
Wastewater Volume (gal)	23,200	27,200	21,600	28,000	
Initial pH	10.2	5.8	7.6	7.5	
Cr <sup>+6</sup> Concentration (mg/L)	0	0	0	0.84	
Lab Sample #	825-5304-1	825-5307-1	825-5307-1	---	
Adjusted pH	7.7	7.4	7.6	7.5	
Sodium Sulfide Volume Added (gal)	1.6	1.8	1.5	1.9	
pH after Sulfide Addition	8.1	7.8	8.2	7.8	
Ferrous volume Added (gal)	3.2	3.4	3.0	3.5 +0.3	
pH After Sulfate Addition	8.0	7.3	7.7	7.5	
Final Adjusted pH	7.7	7.4	7.7	7.5	
Final Cr <sup>+6</sup> Concentration (mg/L)	0	0	0	0	
Comments	PO <sub>4</sub> = 13.45 ppm	PO <sub>4</sub> = 4.9 ppm	PO <sub>4</sub> = 12.9 ppm	PO <sub>4</sub> = 16.5 ppm	

# Treatment Log

Date	11/17/95	11/22/95	11/28/95	11/29/95
Time	7:00	10:45	7:00	9:30
Batch #	825-5321	825-5326	825-5332	825-5333
Operator	PGL & RR	PGL & RR	RR/JK	
Wastewater Volume (gal)	24,000	32,000	37,600	28,000
Initial pH	2.1	5.0	2.6	2.8
Cr <sup>+6</sup> Concentration (mg/L)	0	0	0.12	0.01
Lab Sample #	825-5321	825-5320-112	825-5332-01	825-5333
Adjusted pH	7.7	7.7	7.6	7.6
Sodium Sulfide Volume Added (gal)	1.6	2.2	2.9	1.9
pH after Sulfide Addition	8.2	8.2	7.6	8.7
Ferrous volume Added (gal)	3.3	4.0	5.0	3.8
pH After Sulfate Addition	7.6	7.7	7.6	7.2
Final Adjusted pH	7.6	7.7	7.6	7.6
Final Cr <sup>+6</sup> Concentration (mg/L)	0	0	0	0
Comments	PO <sub>4</sub> = 21.69 ppm	PO <sub>4</sub> = 25.31 ppm		



Treatment Log					
Date	12/1/95	12/5/95	12/8/95	12/12/95	
Time	07:00	10:00	07:45	07:30	
Batch #	825-5335	825-5339	825-5342	825-5353	
Operator	JK	PGL	PGL		
Wastewater Volume (gal)	28,000	23,200	23,200	18,400	
Initial pH	2.4	3.8	7.5	7.1	
Cr <sup>+6</sup> Concentration (mg/L)	0.0	0	0	0.15	
Lab Sample #	12/1/95	NA	NA		
Adjusted pH	7.5	7.6	7.5	7.5	
Sodium Sulfide Volume Added (gal)	1.9	1.6	1.6	1.2	
pH after Sulfide Addition	7.7	8.5	8.4	8.1	
Ferrous volume Added (gal)	3.8	3.2	3.2	2.6	
pH After Sulfate Addition	7.4	7.6	7.7	7.5	
Final Adjusted pH	7.4	7.6	7.7	7.5	
Final Cr <sup>+6</sup> Concentration (mg/L)	0.0	0.0	0.0	0.0	
Comments	PO <sub>4</sub> = 19.12	PO <sub>4</sub> = 15.97			

# Treatment Log

Date	12/14/95	12/18/95	
Time	08:30	07:30	
Batch #	5348	825-5352	
Operator	JK	PGL	
Wastewater Volume (gal)		25,600	
Initial pH	1.8	9.6	
Cr <sup>+6</sup> Concentration (mg/L)	0.0	0.00	
Lab Sample #	5348/12/14/95	82505352-1	
Adjusted pH	7.5	7.6	
Sodium Sulfide Volume Added (gal)	1.5	1.7	
pH after Sulfide Addition	7.8	7.7	
Ferrous volume Added (gal)	3.8	3.5	
pH After Sulfate Addition	7.2	7.6	
Final Adjusted pH	7.5	7.6	
Final Cr <sup>+6</sup> Concentration (mg/L)	0.00	0.00	
Comments	PO <sub>4</sub> = 3.7	PO <sub>4</sub> = 4.44	

Treatment Log				
Date	1/2/96	1/9/96		
Time	07:00	06:30		
Batch #	6002	6009		
Operator	PGL & LL	JK		
Wastewater Volume (gal)	37,600	25,600		
Initial pH	7.2	5.9		
Cr <sup>+6</sup> Concentration (mg/L)	0	0.01		
Lab Sample #	825-6002-1	NONE		
Adjusted pH	7.2	7.2		
Sodium Sulfide Volume Added (gal)	2.6	1.7		
pH after Sulfide Addition	8.1	7.8		
Ferrous volume Added (gal)	5.0	3.2		
pH After Sulfate Addition	7.6	7.4		
Final Adjusted pH	7.6	7.4		
Final Cr <sup>+6</sup> Concentration (mg/L)	0	0		
Comments	PO <sub>4</sub> = 8.92	PO <sub>4</sub> = 12.56		

Treatment Log				
Date	2/10/96	2/14/96	2/20/96	
Time	14:00	07:30	09:00	
Batch #	825-6041	825-6045	825-6051	
Operator	R. ROTMARK	BLD	BLD	
Wastewater Volume (gal)	38,200	36,000	28,800	
Initial pH	11.6	9.20	12.12	
Cr <sup>+6</sup> Concentration (mg/L)	0.3	0.66	0.66	
Lab Sample #	825-6040 2/9/96		825-6051-01	
Adjusted pH	7.6	7.5	7.5	
Sodium Sulfide Volume Added (gal)	2.7	4.9	2.4	
pH after Sulfide Addition	7.8	7.8	7.6	
Ferrous volume Added (gal)	5.2	9.3	4.6	
pH After Sulfate Addition	7.8	7.8	7.5	
Final Adjusted pH	7.61	7.8	7.5	
Final Cr <sup>+6</sup> Concentration (mg/L)	0	0	0	
Comments			1 DRUM SLUDGE	

Treatment Log						
Date	3/07/96	3/14/96	3/21/96	3/27/96		
Time	09:45	14:00	07:30	09:45		
Batch #	6067	6074	6081	6087		
Operator	Bob	Bob	Bob	Bob		
Wastewater Volume (gal)	25,600	36,800	32,000	32,800		
Initial pH	3.07	5.16	3.16	1.53		
Cr <sup>+6</sup> Concentration (mg/L)	6.6	0.06	7	2.6		
Lab Sample #		825-6074-1 3/14/96	825-6081-01 3/21/96	825-6087-4 3/27/96		
Adjusted pH	7.5	7.2	7.39	7.5		
Sodium Sulfide Volume Added (gal)	11.8	2.5	5.8	3.9		
pH after Sulfide Addition	8.0	7.5	7.74	7.73		
Ferrous volume Added (gal)	21.4	4.6	11.2	7.7		
pH After Sulfate Addition	7.9/8.6	7.3	7.6	7.7		
Final Adjusted pH	7.4	7.3	7.6	7.8		
Final Cr <sup>+6</sup> Concentration (mg/L)		0				
Comments	PO <sub>4</sub> = 14.48	PO <sub>4</sub> = 14.39	PO <sub>4</sub> = 4.07	PO <sub>4</sub> = 2.55		

Treatment Log					
Date	4/3/96	4/9/96	4/10/96	4/16/96	
Time	07:00	08:30	06:45	08:00	
Batch #	6094	6100	6100	825-6107	
Operator	Bob	Bob	Bob	PGL	
Wastewater Volume (gal)	29,600	35,200	35,200	39,200	
Initial pH	6.67	6.87		7.41	
Cr <sup>+6</sup> Concentration (mg/L)	3.9	0.52		0.66	
Lab Sample #	826-6044-04	825-6100-01			
Adjusted pH	7.8			7.41	
Sodium Sulfide Volume Added (gal)	2.6	2.5		2.7	
pH after Sulfide Addition					
Ferrous volume Added (gal)	4.0	4.5		5.0	
pH After Sulfate Addition				7.56	
Final Adjusted pH		7.6	7.5	7.56	
Final Cr <sup>+6</sup> Concentration (mg/L)		0		0	
Comments	PO <sub>4</sub> = 19.85	PO <sub>4</sub> = 23.86	PO <sub>4</sub> =	PO <sub>4</sub> = 16.55	

Treatment Log					
Date	4/23/96	4/26/96	5/1/96	5/8/96	
Time	08:15	07:30	12:15	07:30	
Batch #	6114	6117	6122	6129	
Operator	Bob	Bob	PGL	Bob	
Wastewater Volume (gal)	35,200	36,800	32,000	32,000	
Initial pH	8.47	8.6	6.38	7.88	
Cr <sup>+6</sup> Concentration (mg/L)	5.2	0.51	0.11	310*	
Lab Sample #		NA	NA	NA	
Adjusted pH			7.55		
Sodium Sulfide Volume Added (gal)	2.5	6.5	2.2	89.6	
pH after Sulfide Addition			7.68		
Ferrous volume Added (gal)	5.3	7.0	4.0	133.0	
pH After Sulfate Addition			7.81		
Final Adjusted pH	7.95		7.81		
Final Cr <sup>+6</sup> Concentration (mg/L)	0		0	0	
Comments	PO <sub>4</sub> = 25.40 ppm	PO <sub>4</sub> = 24.67 ppm		PO <sub>4</sub> = 26.70 ppm	
		1 Drum Sludge		*Unscheduled Discharge	

# Treatment Log

Date	5/13/96	5/17/96	5/21/96	5/24/96
Time	07:30	08:00	08:00	07:30
Batch #	6134	6138	6142	6145
Operator	Bob	Bob	Bob	Bob
Wastewater Volume (gal)	34,400	39,200	31,200	28,200
Initial pH	12.55	8.9	8.9	8.8
Cr <sup>+6</sup> Concentration (mg/L)	21.0	100.0	11.0	8.0
Lab Sample #	NA	6138-1	NA	NA
Adjusted pH	7.5	7.5	7.6	7.7
Sodium Sulfide Volume Added (gal)	6.0	26.1	12.4	5.2
pH after Sulfide Addition				
Ferrous volume Added (gal)	8.3	49.0	16.6	9.0
pH After Sulfate Addition	7.3			
Final Adjusted pH	7.9		8.4	
Final Cr <sup>+6</sup> Concentration (mg/L)	0	0	0	
Comments	PO <sub>4</sub> = 3.1			PO <sub>4</sub> = 22.5 ppm
	1/4 Drum Sludge	1.25 Drum Sludge	1/4 Drum Sludge	1.75 Drum Sludge



Treatment Log					
Date	6/5/96	6/11/96	6/20/96	6/26/96	
Time	07:45	06:00	06:30	06:30	
Batch #	6157	6163	6172	6176	
Operator	Bob	Bob	Bob	Bob	
Wastewater Volume (gal)	29,600	32,000	34,400	29,600	
Initial pH	7.7	8.5	9.1	8.5	
Cr <sup>+6</sup> Concentration (mg/L)	12.0	2.4	0.04	5.0	
Lab Sample #		NA	NA	825-6178-2	
Adjusted pH		7.6	7.8	7.8	
Sodium Sulfide Volume Added (gal)	12.9	2.2	8.5	5.0	
pH after Sulfide Addition		7.6			
Ferrous volume Added (gal)	20.0	4.4	13.0	10.0	
pH After Sulfate Addition		7.6			
Final Adjusted pH		7.6	7.8		
Final Cr <sup>+6</sup> Concentration (mg/L)		0	0	0	
Comments			PO <sub>4</sub> = 24.34 ppm	PO <sub>4</sub> = 153.3	
		2 Drum Sludge		5 Drums Cr & Water	

# Treatment Log

Date	7/8/96	7/15/96	7/18/96	7/26/96
Time	08:00	07:30	08:00	13:00
Batch #	6190	6197	62,000	6206
Operator	Bob	Bob	Bob	Knuth
Wastewater Volume (gal)	27,200	37,600	31,200	36,000
Initial pH	8.4	8.6	9.7	7.9
Cr <sup>+6</sup> Concentration (mg/L)	4.9	4.91	21.0	0.04
Lab Sample #	NA	825-6197-1		
Adjusted pH	7.5	7.6	7.4	7.4
Sodium Sulfide Volume Added (gal)	3.4	6.5	16.3	3.4
pH after Sulfide Addition	7.6			7.3
Ferrous volume Added (gal)	5.5	10.7	27.5	4.8
pH After Sulfate Addition	7.0			7.3
Final Adjusted pH		7.6	7.4	7.4
Final Cr <sup>+6</sup> Concentration (mg/L)	0	0		0
Comments	PO <sub>4</sub> = 29.92	PO <sub>4</sub> = 21.95	PO <sub>4</sub> = 29.01	

Treatment Log					
Date	7/29/96	8/2/96	8/7/96	8/12/96	
Time	07:30	07:00	07:00	07:15	
Batch #	6211	6215	6220	6225	
Operator	Bob	Bob	Bob	Bob	
Wastewater Volume (gal)	33,600	40,000	39,200	30,400	
Initial pH	7.1	8.3	7.1	7.0	
Cr <sup>+6</sup> Concentration (mg/L)	0.01	7.0	0.01	7.0	
Lab Sample #					
Adjusted pH		7.3	7.1	7.2	
Sodium Sulfide Volume Added (gal)	0.5	7.0	2.6	7.1	
pH after Sulfide Addition	7.1	7.6			
Ferrous volume Added (gal)	1.4	11.0	4.9	11.6	
pH After Sulfate Addition	7.1				
Final Adjusted pH	7.1	8.1	6.9	7.2	
Final Cr <sup>+6</sup> Concentration (mg/L)	0	0	0	0	
Comments	PO <sub>4</sub> = 27.14	PO <sub>4</sub> = 23.28	PO <sub>4</sub> = 24.47		

**APPENDIX D**

**SAMPLE OF CLARIFICATION DATA AND SLUDGE COLLECTION LOGS**

**AT THE NUWC IWTP**

# Clarification Log

Date	12/4/95	12/6/95	12/6/95	12/8/95
Time	09:00	07:00	12:30	08:45
Batch Number	5335	5339	5339	5342
Operator	PGL	PGL	PGL	PGL
Flowrate (gpm)	45	45	50	40
1120 Polymer Make Up Volume (gal)	7	25	8	9
1120 Polymer Pump Rate (%)	80	80	80	80
1195 Polymer Pump	50	50	50	50
Settings	60	60	60	60
P54 Speed	EXT 60	EXT 50.5	EXT 0.1	EXT 10.0
Streaming Current	-0.04 MAN	-0.02 AUTO	+0.01 AUTO	1.27 MAN
Turbidity (FTU)	1.57	1.59	1.53	1.27
Sludge Depth				
Sludge Volume Wasted (gal)		YES		
Effluent Sample No.				
Comments		1/4 DRUM		

Clarification Log					
Date	3/22/96	3/26/96	3/27/96	3/28/96	
Time	06:30				
Batch Number	6081		6087	6087	
Operator	John				
Flowrate (gpm)	60			50	
1120 Polymer Make Up Volume (gal)	30/300		1160X polymer		
1120 Polymer Pump Rate (%)	80	80	80	80	
1195 Polymer Pump Settings	P55 Speed				
	P54 Stroke				
	P54 Speed				
Streaming Current					
Turbidity (FTU)	3.54	Needs Calibrated	Needs Calibrated Very Clear	Needs Calibrated Very Clear	
Sludge Depth					
Sludge Volume Wasted (gal)			yes	yes	
Effluent Sample No:	pH 7.6				
Comments	1 1/2 Drum		1/4 Drum	1/4 Drum	

Sludge Wasted (see Treatment Logs)

As of 29 November 1¼ drums of sludge

1 Dec - 12 Dec - ½ drum

14 Dec - 18 Dec 1 drum

through 18 Dec ~ 3 drums.

Drums on Dock waiting to be shipped				
# 1	Accumulation	Start	Date	10/4/95
# 2	Accumulation	Start	Date	11/22/95
# 3	Accumulation	Start	Date	11/29/95
# 4	Accumulation	Start	Date	12/22/95
# 5	Accumulation	Start	Date	1/9/96
# 6	Accumulation	Start	Date	2/9/96
# 7	Accumulation	Start	Date	2/16/96
# 8	Accumulation	Start	Date	2/22/96
# 1 through 4 are full drums. # 5 1/3 full as of 1/17/96				

Further Treatment log sludge wasted 2 Jan to 25 Jan = 1 drum

10-22 Feb = 1 drum

Full Drums on Dock Waiting to be Shipped	
Drum	Date
# 9	2/26/96
# 10	3/04/96
# 11	3/08/96
# 12	3/18/96
# 13	3/21/96
# 14	3/27/96
# 15	4/02/96
# 16	4/09/96
# 17	4/10/96
# 18	4/26/96
# 19	4/29/96
# 20	5/13/96
# 21	5/16/96
# 22	5/17/96
# 23	5/28/96
# 24	5/29/96
# 25	6/10/96
# 26	6/11/96
# 27	6/14/96
# 28	6/24/96
Drum # 1 was primarily hydroxide sludge	



Comparison of sludge generated using FS/SS process with hydroxide process during periods of high chromium additions of sodium dichromate. (25 gallons of high  $\text{Cr}^{+6}$  added per drop ( $\approx 600 \text{ mg/L Cr}^{+6}$ ))

FS/SS	
Date	Flowmeter Reading
1/25/96	7,145,950 gallons
4/24/96	7,583,330 gallons
Water Processed	437,380 gallons
1/23/95	4,185,300 gallons
3/7/95	4,620,630 gallons
Water Processed	435,330 gallons
Sludge Wasted	
1/24/95	4 drums
2/14/95	1 drum
2/23/95	2 drums
3/16/95	3 drums
Total	10 drums
These are dates when logged in at disposal	

APPENDIX E

SAMPLES OF ANALYTICAL DATA


(SAMPLE ID NUMBERS CORRESPOND TO THE BATCH NUMBERS IN APPENDIX C)

SS/FS PROCESS AT THE NUWC IWTP

NAVAL UNDERSEA WARFARE CENTER DIVISION KEYPORT  
CODE 532 MATERIALS ANALYSIS DIVISION  
ANALYTICAL CHEMISTRY REPORT

Lab No.

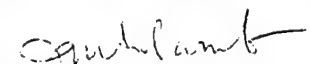

C-247-95

Customer's Name John Knuth	Code 0432	Phone 6-2119	Date Submitted 3-20-95	Analyst(s) JG																										
Job Order Number 6533602	Weapon/Program Hazardous Waste		Sampling Method Grab																											
Sample Name Pretreatment Chromium Reactor Waste	Date Sampled 3-20-95		Sample ID Number 5079-01																											
Location Bldg. 825	Drum Number N/A		Lab Notebook Number 5322-28.1																											
Background and Description of Service(s) Requested Priority Pollutant Metals																														
Physical Characteristics pH @ 25°C: N/A Flash Point, °F: N/A Layers: N/A																														
Organics Detergents (LAS), mg/L: N/A TPH, Recoverable, mg/L: N/A		Inorganics Total Priority Pollutant Metals: <table border="1"> <thead> <tr> <th>Elements</th> <th>Results, mg/L</th> </tr> </thead> <tbody> <tr><td>Chromium</td><td>37</td></tr> <tr><td>Nickel</td><td>7</td></tr> <tr><td>Cadmium</td><td>&lt;1</td></tr> <tr><td>Lead</td><td>&lt;1</td></tr> <tr><td>Zinc</td><td>1</td></tr> <tr><td>Copper</td><td>&lt;1</td></tr> <tr><td>Silver</td><td>&lt;1</td></tr> <tr><td>Antimony</td><td>&lt;1</td></tr> <tr><td>Beryllium</td><td>&lt;1</td></tr> <tr><td>Arsenic</td><td>3</td></tr> <tr><td>Selenium</td><td>&lt;1</td></tr> <tr><td>Thallium</td><td>&lt;1</td></tr> </tbody> </table>			Elements	Results, mg/L	Chromium	37	Nickel	7	Cadmium	<1	Lead	<1	Zinc	1	Copper	<1	Silver	<1	Antimony	<1	Beryllium	<1	Arsenic	3	Selenium	<1	Thallium	<1
Elements	Results, mg/L																													
Chromium	37																													
Nickel	7																													
Cadmium	<1																													
Lead	<1																													
Zinc	1																													
Copper	<1																													
Silver	<1																													
Antimony	<1																													
Beryllium	<1																													
Arsenic	3																													
Selenium	<1																													
Thallium	<1																													
Unused Sample Returned <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No <input type="checkbox"/> N/A		1 Per SW-846, EPA Method 6010A.																												
Oral Results Reported To: Date:	 Reviewed By Date: 3/27/95		Jimi Luthrie 3-27-95 Analyst Date Phone: (206) 396-2501 x296																											

NAVAL UNDERSEA WARFARE CENTER, DIVISION KEYPORT  
CODE 532 MATERIALS ANALYSIS DIVISION  
ANALYTICAL CHEMISTRY REPORT

Lab Number

C-74-96

Customer's Name P. G. Lingenfelter	Code 0432	Phone 6-2119	Date Submitted 10-23-95	Analyst(s) JG
Job Order Number 6533602	Weapon/Program Hazardous Waste		Sampling Method Grab	
Sample Name Chrome Reactor Sodium Sulfide R&D	Date Sampled 10-20-95		Sample ID Number 825-5293-1	
Location Bldg. 825	Drum/Tank Number N/A		Lab Notebook Number 5322-28.89	
Background and Description of Service(s) Requested Priority Pollutant Metals, iron, and aluminum				
Physical Characteristics: N/A				
Purgeable Volatiles, mg/L: N/A		<u>Total Priority Pollutant Metals,</u> mg/L:  silver <1 arsenic <1 beryllium <1 cadmium <1 chromium 3 copper 1 nickel <1 lead <1 antimony <1 selenium <1 thallium <1 zinc 1  aluminum, mg/L: 7 iron, mg/L: 8   1 Per EPA SW-846, Method 3010A/6010A.		
Unused Sample Returned: Yes				
Oral Results	 Reviewed By Date: 10/27/95		 Analyst Date 10-27-95 Ph No. (360) 396-2501 X 296	
Reported To: N/A				
Date: N/A				

NAVAL UNDERSEA WARFARE CENTER, DIVISION KEYPORT  
CODE 532 MATERIALS ANALYSIS DIVISION  
ANALYTICAL CHEMISTRY REPORT

Lab Number  
C-90-96

Customer's Name P. G. Lingenfelter	Code 0432	Phone 6-2119	Date Submitted 10-31-95	Analyst(s) JG
Job Order Number 6533602	Weapon/Program Hazardous Waste		Sampling Method Grab	
Sample Name Chrome Reactor Pretreatment	Date Sampled 10-31-95		Sample ID Number 825-5304-1	
Location Bldg. 825	Drum/Tank Number N/A		Lab Notebook Number 5322-28.90	
Background and Description of Service(s) Requested Priority Pollutant Metals, iron and aluminum				
Physical Characteristics: N/A				
Purgeable Volatiles, mg/L: N/A		<u>Total Priority Pollutant Metals,</u> mg/L:  silver 1 arsenic <1 beryllium <1 cadmium 2 chromium 1 copper <1 nickel <1 lead <1 antimony <1 selenium <1 thallium <1 zinc <1  'aluminum, mg/L: 4 'iron, mg/L: 11   1 Per EPA SW-846, Method 3010A/6010A.		
Unused Sample Returned: Yes				
Oral Results Reported To: N/A Date: N/A	<i>Applicant</i> Reviewed By Date: 11/2/95		<i>Jim Guthrie</i> 11-2-95 Analyst Date Ph No. (360)396-2501 X 296	

NAVAL UNDERSEA WARFARE CENTER, DIVISION KEYPORT  
CODE 532 MATERIALS ANALYSIS DIVISION  
ANALYTICAL CHEMISTRY REPORT

Lab Number

C-362-96

Customer's Name Bob Damiano	Code 0432	Phone 6-2119	Date Submitted 3-27-96	Analyst(s) JG
Job Order Number 6533602	Weapon/Program Hazardous Waste		Sampling Method Grab	
Sample Name Chrome Reactor Pretreatment	Date Sampled 3-27-96	Date Tested 3-28-96, 3-29-96		
Location Bldg. 825	Sample ID Number 825-6087-01	Lab Notebook Number 5322-34.39		

Background and Description of Service(s) Requested

Priority Pollutant Metals, iron and aluminum

Physical Characteristics: N/A

Purgeable Volatiles, mg/L: N/A

Total Priority Pollutant Metals,  
mg/L:

silver	<1
arsenic	<1
beryllium	<1
cadmium	4
chromium	16
copper	2
nickel	1
lead	3
antimony	<1
selenium	<1
thallium	<1
zinc	2

aluminum, mg/L: 9  
iron, mg/L: 26

1 Per EPA SW-846, Method 3015/6010A.

Unused Sample Returned: Yes

Oral Results

Reported To: N/A  
Date: N/A

Reviewed By  
Date: 4/1/96

Analyst  
Date  
Ph No. (360) 396-2501 X 296

NAVAL UNDERSEA WARFARE CENTER, DIVISION KEYPORT  
610 Dowell Street, Keyport, WA 98345  
CODE 532 CHEMISTRY TEST REPORT

Lab Number  
C-374-96

Customer's Name Bob Damiano	Code 0432	Phone 6-2119	Date Submitted 4-3-96	Analyst(s) JG
Job Order Number 6533602	Weapon/Program Hazardous Waste		Sampling Method Grab	
Sample Name Chrome Reactor Pretreatment	Date Sampled 4-3-96		Date Tested 4-15-96	
Location Bldg. 825	Sample ID Number 825-6094-04		Lab Notebook Number 5322-34.46	

Background and Description of Service(s) Requested

Priority Pollutant Metals, iron and aluminum

Physical Characteristics: N/A

Purgeable Volatiles, mg/L: N/A

Total Priority Pollutant Metals,  
mg/L:

silver	<1
arsenic	<1
beryllium	<1
cadmium	1
chromium	19
copper	2
nickel	5
lead	2
antimony	<1
selenium	1
thallium	<1
zinc	5

aluminum, mg/L: 49

iron, mg/L: 72

1 Per EPA SW-846, Method 3015/6010A.

Unused Sample Returned: Yes

Oral Results

Reported To: N/A  
Date: N/A

Reviewed By  
Date: 4/16/96

Analyst

Ph No. (360)396-2501 X 296

4-15-96

Date

NAVAL UNDERSEA WARFARE CENTER, DIVISION KEYPORT  
610 Dowell Street, Keyport, WA 98345  
CODE 532 CHEMISTRY TEST REPORT

Lab Number

C-445-96

Customer's Name Bob Damiano	Code 0432	Phone 6-2119	Date Submitted 5/17/96	Analyst(s) JB
Job Order Number 6533602	Weapon/Program Hazardous Waste		Sampling Method Grab	
Sample Name Chrome Reactor Pretreatment	Date Sampled 5/16/96	Date Tested 6/10/96 & 6/12/96		
Location Bldg. 825	Sample ID Number 6138-1	Lab Notebook Number 5322-33.90		
Background and Description of Service(s) Requested Priority Pollutant Metals, iron and aluminum				
Physical Characteristics: N/A				
Test Parameter(s)		Test Parameter(s) Total Priority Pollutant Metals, mg/L:  silver <1 arsenic <1 beryllium <1 cadmium <1 chromium 20 copper <1 nickel 1 lead <1 antimony <1 selenium <1 thallium <1 zinc 6  aluminum, mg/L: 15 iron, mg/L: 24  1 Per EPA SW-846, Method 3010A/6010A.		
Unused Sample Returned: Yes				
Oral Results	Reviewed By <i>Jimi Guthrie</i> Date: 6/18/96		Analyst <i>J. Brubaker</i> Date 6/18/96 Ph No. (360) 396-2501 X 208	
Reported To: N/A				
Date: N/A				



## APPENDIX F

### SS/FS PROCESS INSTRUMENTATION/CONTROLS SPECIFICATIONS

## KESSLER - ELLIS BATCH CONTROLLER FOR SULFIDE AND FERROUS

### Housing:

High impact plastic case with NEMA 4 front panel.

### Dimensions:

Reference Figure 1-1 (pg 8)

### Display:

8 Digit, 0.55" High, 15 Segment, Red Orange, LED.

### Input Power:

A: 110 VAC  $\pm$  15% or 12 to 27 VDC

B: 220 VAC  $\pm$  15% or 12 to 27 VDC

### Current:

Maximum 280 mA DC or 5.3 VA at rated AC voltage.

### Output Power:

(On AC powered units only): +12 VDC at 100 mA. Separate Isolated 12 VDC at 100 mA to allow  $\pm$  12 VDC or +24 VDC, regulated  $\pm$  5% worst case.

### Temperature:

Operating: +32°F (0° C) to +130 ° F (+54° C)

Storage: -40°F (-40° C) to +200 ° F (+93° C)

### Memory:

EEPROM stores all program, display mode and count data for a minimum of 10 years if power is lost.

### Accuracy over full temperature range:

Analog - Zero error:  $\pm$ 0.175% full scale maximum

Overall error:  $\pm$ 0.5% full scale maximum.

Digital - 100% (within specified voltage ranges)

(Math for factor calculation uses 8 digit floating decimal)

### Reset

Front push button: "CLR" resets displayed number and control output.

### Stop/Reset Remote Input (Terminal 5):

Open or 0 to 1 VDC (low), 4 to 30 VDC (high), 10K ohm input impedance to ground. Minimum pulse on / off time 5 msec.

When activated, the unit will "stop" (if unit is started and the batch is not complete). When the unit is stopped or the batch is complete, a pulse will reset the counter. If pin 5 is held high (4 to 30VDC), all start inputs will be inhibited.

### Start Remote Input (Terminal 10):

Open or 0 to 1 VDC (low), 4 to 30 VDC (high), 10K ohm input impedance to ground. Minimum pulse on / off time 12.5 msec.

Pin 10 is the START input. The unit will "start" on the rising edge if Pin 5 (Stop/Reset) is not held high.

# **DATA INDUSTRIAL CORP. FLOW SENSOR FOR FERROUS AND SULFIDE**

## **Specifications**

### **Wetted Materials**

#### **SENSOR HOUSING AND ENHANCING JET (If Applicable)**

**PVC** - Virgin polyvinyl chloride, Type 1, Grade 1

**PVDF** - Virgin polyvinylidene fluoride

#### **O-RINGS**

**Viton®** - registered trademark of E.I. du Pont Nemours Company

**EPDM**

**Kalrez®** - registered trademark of E.I. du Pont Nemours Company

**Silicon** - Food Grade

**Neoprene**

**Chemraz®** - registered trademark of Greene Tweed Company

**Teflon Encapsulated Viton**

#### **IMPELLER SHAFTS**

**Zirconia Ceramic**

**Hastelloy** - C-276

**Tungsten Carbide** - GE Carboloy 883 cobalt binder

**Titanium** - Titanium Alloy 86Ti-6AL-6V-25A

**Alumina Ceramic** - Diamonite Grade P3142-1

**Monel** - Grade K500

**Stainless Steel** - 316 Stainless Steel

**Tantalum** - Commercial Grade

#### **PROCESS CONNECTIONS**

**PVC** (Virgin polyvinyl chloride, Type 1, Grade 1) schedule 80 tail pieces

**PVDF** (Virgin polyvinylidene fluoride) sockets

**PVDF** union thread (For joining existing piping systems with GF unions)

**PVDF** union nuts with socket union ends

**PVDF** union nuts with 316 stainless steel FNPT union ends

**PVDF** flanges

**PVDF** union nuts with CPVC socket union ends

#### **IMPELLER AND BEARING**

**Tefzel®** - registered trademark of E.I. du Pont Nemours Company

#### **Pressure, Temperature Ratings**

- Depends on hardware configurations. See Diagram at end of this section.

#### **Operating Flow Range**

- 0 to 30 ft/sec for standard range units
- 0 to 10 ft/sec for enhanced flow range units

#### **Recommended Design Flow Range**

- 1 to 20 ft/sec for standard range units to maintain calibration accuracy
- 0.25 to 8 ft/sec for enhanced flow range units to maintain calibration accuracy

## ROSEMONT TURBIDITY SYSTEM

### SPECIFICATIONS

Range	0-200 Nephelometric Turbidity Units (NTU)
Accuracy	$\pm 2\%$ of reading from 0-60 NTU; $\pm 5\%$ of reading from 60-200 NTU
Resolution	0.001 NTU below 1 NTU
Repeatability	Better than $\pm 1.0\%$ reading or $\pm 0.003$ NTU or $\pm 1$ LSD whichever is greater.
Response Time	For a full step change, initial response in 2-1/2 minutes, 90% response in 5 minutes at 750 mL/min flow rate.
Sample Flow Required	250-750 mL/minute (3.5 to 11.5 gph)
Sample Temperature Range	0°C to 60°C
Operating Temperature Range	-10°C to 50°C
Outputs	Isolated 0/4-20 mA or 0-5 VDC with programmable span over $\pm 200$ NTU range. Optional RS232 plus non-isolated 0-5 VDC also with programmable span.
Alarms	2 SPST normally open contacts with 5 amps, 240 VAC contact rating. Configurable for HI-HI, LO-LO, HI-LO with adjustable deadband. Configurable normally closed with circuit jumper change.
Power Requirements	120/240 VAC, 50/60 Hz jumper selectable, 11 Watts max.
Sample Inlet Fitting	1/4" NPT female 1/4" hose barb provided.
Drain Fitting	3/8" NPT female 1/2" hose barb provided.
Control Unit Case	NEMA-4X watertight, dust tight, corrosive resistant
Dimensions	W x H x D
Control Unit	5.75"W x 4.45"H x 6.95"D (146 mm x 113 mm x 177 mm)
Turbidimeter Body	8.25"W x 21.5"H x 4.75"D (210 mm x 546 mm x 121 mm)
Mounting	Panel and wall mount options available
Shipping Weight	11.3 kg (25 lbs.)
Display	3 digit LCD with 2 alarm and 6 caret type annunciators 1/2" character height.
Measurement Averaging	Dampening in fixed steps of 0, 6, 30, 60, 90 seconds of time averaging.

## CHEMTRAC SYSTEMS INC. STREAMING CURRENT DETECTOR

The instrument shall be a streaming current transmitter that continuously measures electrical charge in a water sample after the stream has been dosed with coagulants which destabilize suspended colloids. The instrument shall be capable of outputting a 4-20 mA reference signal which indicates a charge value that corresponds to optimum coagulant dose.

The system shall be two modules (sensor and transmitter) capable of 1000 feet separation. Both modules require 110 VAC power:

### MODULE I - SENSOR

The sensor shall receive a sample at the rate of 5 gallons per minute to ensure sample line cleanliness and sensor cell reliability. The sensor shall have sample exit orifice larger than entrance orifice to avoid pressurizing the cell. The sensor shall not contain any signal processing circuitry or electronic circuit cards. The sensor response time shall not be greater than 2 seconds at recommended sample flow rate. The sensor shall have a high flow, self-cleaning cell that does not require any extra cleaning devices. Sample must enter cell from the side and exit at a 45 degree downward angle to prevent accumulation of grit, sludge, sand, etc. The probe assembly shall be a quick disconnect type for ease of maintenance. The unit shall come standard with one spare replacement probe cartridge. Stainless steel electrodes located in the top and bottom of electrode module shall transmit the generated signal through shielded coaxial cable to the transmitter. A timing signal from an optoelectric device in the sensor module shall be transmitted through a shielded, twisted pair, wire to the transmitter.

### MODULE II - TRANSMITTER

The transmitter shall contain all circuitry and signal processing cards to provide outputs of 4-20 mADC, 0-10 VDC, and  $\pm 10$  VDC. All outputs shall be integral in the transmitter circuitry, and not require any external devices. The transmitter shall have control functions as follows: (1) Meter zero adjustment, full scale on all ranges. (2) Signal gain switch adjustable 1X, 2X, 5X, 10X, 20X. (3) Internal, continuous adjustment for higher gain. (4) Flashing LED sensor operation light. Transmitter shall have wall mount or panel flush mount option.

The instrument shall be a Streaming Current Transmitter Model SCT 1500XR as manufactured by Chemtrac Systems, Inc. Norcross, Georgia.

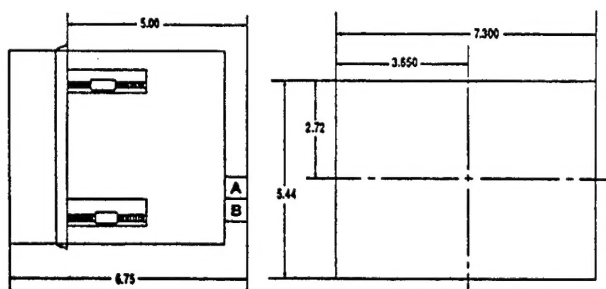
### I. REMOTE SENSOR

Power.....	115 VAC, 60 Hz (standard) 230 VAC, 50 Hz (optional)
Sample Flow Rate.....	5.0 Gal/Min, Max
Sample Cell Type.....	External Receiver, High Flow
Probe Type.....	Quick Replacement Cartridge
Water Sample Connections.....	Inlet-3/4" O.D., Barb Type Outlet-1" O.D.
Materials Contacting Sample.....	Delrin, Nylon, Neoprene Viton, PVC, Stainless Steel
Output Wiring.....	1 ea. Coaxial RG-59/U, 22 AWG 1 ea. Shielded, Twisted Pair, 22 AWG
Enclosure Type.....	Nema 4X, Polycarbonate
Module Size.....	7.40" W, 14.14" H, 5.47" D
Weight.....	10 Pounds
Mounting Holes.....	7.66" x 7.66"
Operating Temperature.....	32 degrees F to 120 degrees F

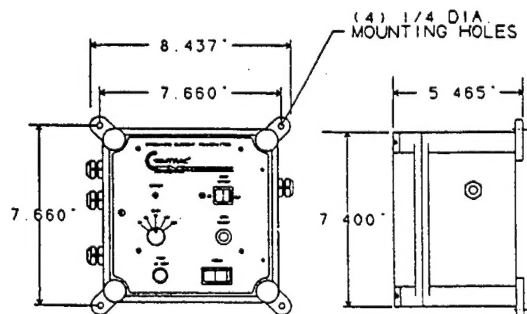
### II. TRANSMITTER

Power.....	115 VAC, 60 Hz (standard) 230 VAC, 50 Hz (optional)
Streaming Current signals.....	4-20mA (600 ohms load) standard 0-10 VDC, standard -10/+10 VDC, standard
Self Diagnostics.....	Sensor Operation LED
Gain Adjustment.....	External, 5 pos. Switch (1X, 2X, 5X, 10X, 20X) Internal, Continuous adjustment for Higher Gain
Zero Adjustment.....	Full Scale All Ranges
Enclosure type.....	Polycarbonate NEMA 4X, Wall Mount, (standard) ABS NEMA I, Panel Mount, (optional)
Weight.....	5 lbs.
Dimensions.....	Wall Mount - 8.5" W x 8.5" H x 5.5" D (Mounting Holes 7.40" W x 7.40" H)

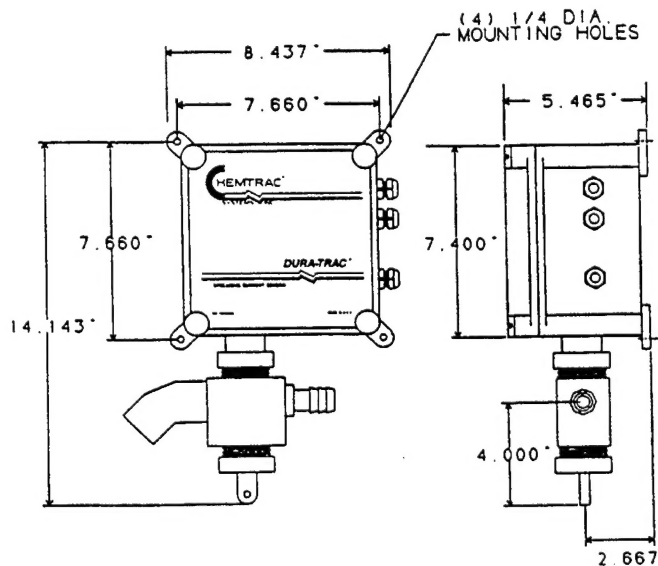
Panel Mount - 7.50" W x 5.50" H x 6.50" D  
(Cutout for Panel Mount 7.30" W x 5.44" H)



PANEL MOUNT TRANSMITTER



WALL MOUNT TRANSMITTER



DURA-TRAC™ SENSOR  
SCM 1500XR MOUNTING & OUTLINE